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Original Research Paper

IR spectroscopic studies on Hofmann-danon-type clathrates: $M(1,9\text{-diaminononane})Ni(CN)_4 \cdot G$ [$M = Co, Ni$ or Cd ; $G = \text{nitrobenzene (NB)}$]

ABSTRACT

IR spectra of three tetracyanonickelate complexes with 1,9-diaminononane as ligand and three of their clathrates with guest nitrobenzene are presented. It is shown that they have similar structures and exhibit weak hydrogen bonding between the π -cloud of aromatic guest and the ligand of the host lattice which is observed in all clathrates. The presence of nitro group in the phenyl ring of guest appears to impart a special affinity with the host due to a second type of hydrogen bonding between the NO_2 of nitrobenzene and the cyanide group of the lattice. The cyanide vibrational frequencies in the present clathrates are found to be in the order $Cd-Ni-G$, $Co-Ni-G$, $Ni-Ni-G$ due to increase in second ionization potential of outer metal ion. Declathration by heating shows that after the elimination of guest, the host lattice is stable since the IR spectra of the heated clathrate sample is the same as its host. So there is only a very weak hydrogen bonding between the host and guest. These empty sites of host are occupied by moisture and retained as clathrated water. The host lattice of clathrates, are found to be similar to those of Hofmann- α, ω -diamino long chain alkane clathrates. The stability of these compounds are based on H-bonds involving NO_2 of nitrobenzene, π cloud of the guest and the cyanide moieties.

Keywords: 1,9-diaminononane, clathrates, FTIR spectra, Hofmann-(en)₂-type, guest-host interactions, nitrobenzene,

1. INTRODUCTION

Guest-host interactions in inclusion compounds such as clathrates are very important in molecular recognition and separation. Majority of inorganic complexes of Hofmann-type and related clathrates exhibit such property compared to clathrates formed by organic host compounds. Guest-host interactions in clathrates, provide explanation for the effects of enclathration on the structural and spectral properties of both the guest and the host molecules and the stability of the particular compounds. Hofmann-type clathrates exhibit such type of interactions, varying from charge transfer forces to weak van der Waals' interactions to hydrogen bonding [1]. Although the interactions are weak in nature, they lead to significant changes in IR, Raman, EPR, NMR and optical spectra of the inclusion compounds.

Following the synthesis of Hofmann-type clathrates of the type, $M(NH_3)_2Ni(CN)_4 \cdot nG$ ($M = \text{divalent metal ion}$; $G = \text{aromatic guest molecule}$), a series of analogous clathrates of general formula,

M(diam)Ni(CN)₄.G (diam = α,ω-diaminoalkane = NH₂(CH₂)_nNH₂) were developed [2,3]. The three-dimensional host lattices of such clathrates have been prepared from the two-dimensional M(NH₃)₂Ni(CN)₄ by replacing the two ammonia molecules opposed to each other between adjacent metal complex sheets of [CdNi(CN)₄]_n by a diaminoalkane which bridges the adjacent sheets. The structure of Cd[NH₂(CH₂)₉NH₂](CN)₄.0.5o-xylene [4] reveals a three-dimensional host framework built of the layers of a two dimensional catena-[cadmium tetra-μ-cyanonickelate] network and of the ambidentate 1,9-diaminononane (danon) bridging the Cd atoms in adjacent networks. The guest o-xylene molecule is accommodated in the cavity formed in the interlayer space. The skeleton of the danon in the Cd-NC9N-Cd linkage takes a (gauche)₂(trans)₈ conformation twisted at the (gauche)₂ part. The twisted (gauche)₂ part of the danon skeleton occupies the interlayer space to such an extent that the stoichiometric number of the guest per formula unit of the host is just 0.5. The model of the Hofmann-diam-type host structure is schematically illustrated in Figure1. Although the IR spectra of Ni(danon)-td-type clathrates have been reported [5] with guest benzene and dichlorobenzene, the only study available on Hofmann-danon-type clathrates concerns with the IR spectra of M(danon)Ni(CN)₄.G (M = Cd or Ni; G=benzene, naphthalene, anthracene or phenanthrene) [2]. Further, the only nitrobenzene clathrate available is cadmium-N-methyl-1,3-diaminopropane tetracyanonickelate(II) 0.5 nitrobenzene [6] which deals with NMR studies.

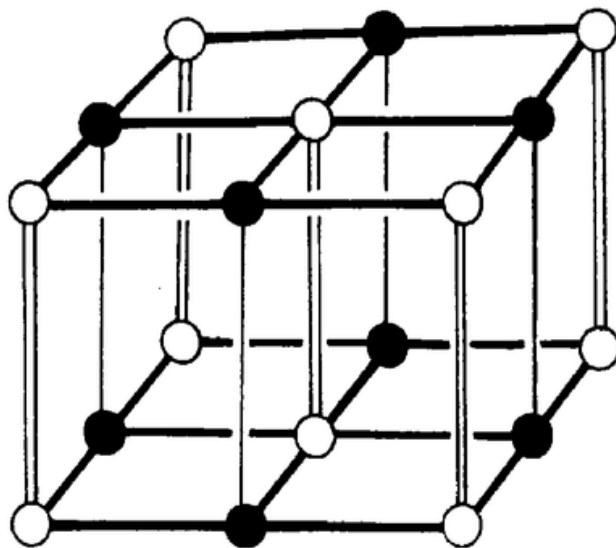


Figure1. The model for the Hofmann-diam-type host structure (open circle: 6-coordinate M, solid circle: square-planar Ni, open column: an ambident ligand, thick line: CN bridge and thin line: edge of cavity).

2. MATERIAL AND METHODS

2.1. Synthesis of K₂[Ni(CN)₄]

All the chemicals were obtained from the commercial sources (Merck, Aldrich) and used without further purification. The host complexes were prepared according to literature method [2,5]. To a

66 solution of nickel sulphate ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$; 5.75 gm in 50 ml water = 20 mmol), a KCN solution (40
67 mmol; 2.60 gm in 50 ml water) was added with constant stirring. A white precipitate of $\text{Ni}(\text{CN})_2$
68 formed was separated and dissolved by adding an excess of KCN solution (40 mmol). The resulting
69 solution was filtered off, concentrated on a water bath and kept undisturbed. Colorless crystals of
70 $\text{K}_2[\text{Ni}(\text{CN})_4]$ appeared within a week. They were collected and dried in an air oven at 110°C for two
71 hours. It was kept in a desiccator.

72 2.2. Synthesis of host complexes: $\text{M}(\text{1,9-diaminononane})\text{Ni}(\text{CN})_4$ (M=Co, Ni or Cd) 20

73 Typically one mmol of $\text{K}_2\text{Ni}(\text{CN})_4$ was dissolved in water (20 mL). To this solution, one mmol of the
74 ligand and one mmol of the metal chloride, dissolved in ethanol (5 mL each), were added with
75 constant stirring. The resultant solution was filtered off and kept undisturbed for slow evaporation. The
76 powdery compounds, obtained in a week's time, were filtered off, washed with water and acetone
77 successively and dried in an air oven at 100°C . Then they were kept in a desiccator containing
78 anhydrous solid calcium chloride. The complexes thus prepared were: $\text{M}(\text{danon})\text{Ni}(\text{CN})_4$ and
79 abbreviated as Ni-Ni (1'), Co-Ni (2') and Cd-Ni (3'). Samples of the compounds were stable at
80 atmospheric temperature and polycrystalline in nature.
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82 2.3. Synthesis of the clathrates by solution method

83 3 mmol of the guest and 1 mmol of danon contained in a solution of ethanol and 1 mmol of aqueous
84 solution of $\text{K}_2\text{Ni}(\text{CN})_4$ were added to a 1 mmol aqueous solution of MCl_2 (M = Co, Ni or Cd) with
85 stirring. The clathrate precipitate formed was filtered, washed with water, ethanol and ether
86 successively and kept in a desiccator containing saturated guest vapour. The clathrates obtained by
87 the above procedure are:
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- 89 $\text{Ni}(\text{danon})\text{Ni}(\text{CN})_4$. Nitrobenzene (1) ; abbreviated as Ni-Ni-NB
- 90 $\text{Co}(\text{danon})\text{Ni}(\text{CN})_4$. Nitrobenzene (2) ; abbreviated as Co-Ni-NB
- 91 $\text{Cd}(\text{danon})\text{Ni}(\text{CN})_4$. Nitrobenzene (3) ; abbreviated as Cd-Ni-NB

92 2.4. Physical Measurements

93 The host complexes, clathrate compounds were analyzed for C, H and N using the CHNS analyzer,
94 Varian Micro cube and LECO CHNS-932 and the metals by atomic absorption spectra. The freshly
95 prepared compounds, 1-3, were analysed for C, H and N and the following results (found %
96 /calculated %) were obtained (Table 1). The results indicate that the number of guest molecules in the
97 present compounds is one. A similar value has been reported for other Hofmann type clathrates too
98 [2,3,7-10]. FT-IR spectra were recorded between $4000\text{-}400\text{cm}^{-1}$ on a JASCO 400-FT-IR spectrometer
99 with the resolution of 4 cm^{-1} . The spectrometer was calibrated using a standard polystyrene film. The
100 samples were prepared as mulls in nujol placed between NaCl discs and as KBr discs. At ambient
101 conditions, the samples decompose, and hence a fresh sample preserved under guest vapours was
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Table1. Results of elemental analysis for 1-3

Compound	C %	H%	N%	Ni%	%
Ni(C ₉ H ₂₂ N ₂)Ni(CN) ₄ . C ₆ H ₅ NO ₂ (1)	45.13/45.38	5.26/5.37	19.32/19.51	23.41/23.36	
Co(C ₉ H ₂₂ N ₂)Ni(CN) ₄ . .C ₆ H ₅ NO ₂ (2)	45.17/45.36	5.45/5.37	19.28/19.50	11.59/11.68	Co =11.65/11.72
Cd(C ₉ H ₂₂ N ₂)Ni(CN) ₄ . .C ₆ H ₅ NO ₂ (3)	40.79/41.00	4.71/4.86	17.46/17.62	10.42/10.56	Cd =20.23/20.22

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3. RESULTS AND DISCUSSION

Due to the flexibility of the host frame-work with long diamine ligand, the number of guest molecules that can be accommodated in the cages is decreased from two, normally observed in Hofmann-en-type clathrates[11] to one in the present clathrates of general formula, M(danon)Ni(CN)₄.G (M = Ni, Co or Cd; G = nitrobenzene). It may be due to the fact that one of the two cavities being occupied by the skeletal carbon-chain with suitable conformation instead of a guest molecule. Similar observations have been made in Hofmann-daon-type clathrates Cd(daon)Ni(CN)₄.G (daon = α,ω-diaminooctane; G = *ortho*- or *para*-toluidine) [12].

3.1. Nitrobenzene Guest vibrations

FT-IR spectra suggests the presence of hydrogen bonding between the amine of host lattice and the pi-electrons of aromatic guest molecules in Hofmann-type clathrates [13]. There are three distinct sets of vibrations in all clathrates. The first one corresponds to those of guest aromatic molecule, second from the ligand molecule and third from the host sheet structure. In relation to liquid guest molecule, shifts of the bands of the guest molecule in the present clathrates 1-3, are very small except a few bands which throw light on the nature and extent of H-bonding. In general, the band assignments of the guest molecule are in good agreement with those found in literature. The typical IR spectra of the clathrate compound, Ni-Ni-NB (1), heated 1 and the host Ni-Ni (1'), are presented in Figure 2. The IR spectra and its nitrobenzene vibrations of the analogous clathrate compound 2 is also presented. The vibrational frequencies and band assignments are given in Table 2. Scrutiny of the data reveals the presence of all characteristic bands of nitrobenzene in the clathrates, 1-3. In the 800-670 cm⁻¹ region, out of plane vibrational modes of the nitrobenzene (793, 703, 676 cm⁻¹) modes show 1-7 cm⁻¹ shifts to higher frequencies compared to liquid nitrobenzene in literature [14,15]. The nitro group and C-N stretching vibrations do not show any shift from liquid nitrobenzene vibrational values in the region of 1523-852 cm⁻¹. Stretching vibrations of C-H and ring C-C modes shift to higher or lower frequencies compared to liquid nitrobenzene in the region 3100-1606 cm⁻¹.

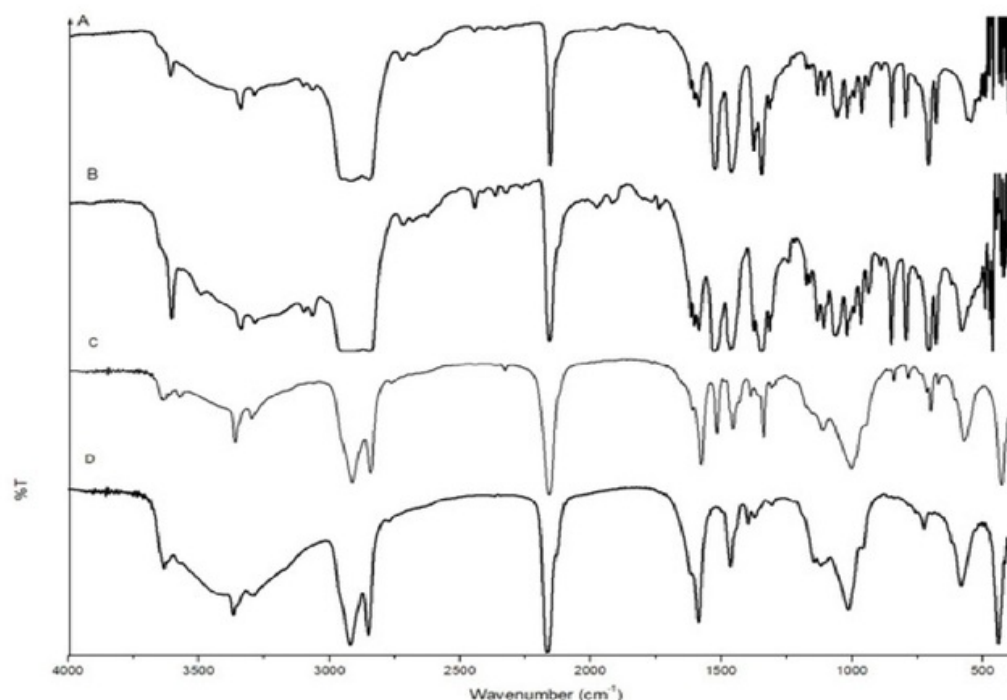


Figure 2. FT-IR spectra of (A) clathrate Co-Ni-NBz (2) in nujol; (B) clathrate Ni-Ni-NBz (1) in nujol; (C) heated (1) in KBr and (D) the host Ni-Ni (1') in KBr.

The $\gamma(\text{CH})$ out of plane deformation mode of aromatic guest normally gets upshifted due to the strain introduced in the cavities or a weak H-bonding with NH_2 of the ligand in the host structure. The corresponding mode of nitrobenzene in **1** shows no shift at 793cm^{-1} but the other modes of $\gamma(\text{CH})$ out of plane at 703 and 676cm^{-1} for the compounds **1-3** show shifts to higher frequencies ($1-7\text{cm}^{-1}$). This shift is small compared to that of benzene in benzene clathrates [2,8]. It may probably be due to the presence of a weak hydrogen bonding between the π cloud of nitrobenzene guest and amino group of ligand in the host lattice. The smaller shifts may be explained due to the larger distance between the layer sheets which effectively separate the ligand molecule from the guest molecule. Therefore, it is suggested that the frequency shifts in our compounds are due to π electron donation from the nitrobenzene ring to the hydrogen atom of the amino group of ligand in the host lattice which has more electrophilic character caused by coordination. Similar observation has been observed in the other Hofmann-danon-type clathrates [10]. Among the three compounds, **1-3**, this type of shift is maximum in **2** and **3**. The above mentioned hydrogen bonding is also evidenced by the shift in $\nu_a(\text{CH})$ and $\nu_s(\text{CH})$ compared to free nitrobenzene values of 3100 and 3080cm^{-1} respectively and also in ν_{ring} (1606cm^{-1}). Further evidence comes from the appearance of new peaks which are noted in Table 2.

Table 2 :The vibrational frequencies (cm^{-1}) of Nitrobenzene in M-danon-Ni-NB clathrates

Assignment ^a	Nitrobenzene ^a	Ni-Ni-NB (1)	Co-Ni-NB (2)	Cd-Ni-NB (3)
$\nu_a \text{ CH}$	3100 m	3106 s	3106 m	3105 w
$\nu_s \text{ CH}$	3080 m	3076 s	3071 m	3071 w

ν CC	1606 m	1605 vs	1604 m	1603 m
ν_a (N=O ₂)	1523 s	1530 s	1524 s	1523 vs
ν_s (N=O ₂)	1347 s	1347 s	1346 vs	1346 s
ν_s (N=O ₂)	1108 m	1107 s	1107 m	1106 m
ν_s (N=O ₂)	1021 m	1020 w	1020 m	1018 m
ν C-N	852 s	850 s	850 m	851 s
γ CH _o .p	793 s	793 s	796 m	797 s
γ CH _o .p	703 s	704 s	710 s	710 vs
γ CH _o .p	676 s	680 s	681 m	681 s

^aTaken from reference[14]

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The spectral features of the clathrates **2** and **3** indicate that they may have similar structures as that of **1**. Clathrates **2** and **3**, exhibit peaks corresponding to γ (CH)_{op} modes which have been slightly shifted upward (7cm⁻¹) than that of liquid NB similar to observations made in **1**. Since nitrobenzene has an aromatic ring which could be easily recognized by the occurrence of γ (CH)_{o.p} mode at 793 cm⁻¹, focus was made on this vibrational mode present at 796 cm⁻¹ in clathrate **2** and 797 cm⁻¹ in **3**.

3.2. Vibrations of 1,9-diaminononane

2 The assignments and the wavenumbers of the fundamental bands of the ligand, danon, observed in the infrared spectra of the compounds under study are given in Table 3 together with the spectral data for danon in CCl₄ for comparison. The IR bands observed for the clathrates, **1-3**, in the range of 3343-3357 cm⁻¹ and 3292-3293cm⁻¹, assigned to the NH₂ asymmetric and symmetric stretching frequencies of danon, are lower than the corresponding values of free ligand in CCl₄ solution (3361 cm⁻¹ and 3325 cm⁻¹ respectively) [2]. The values are characteristic of coordinated NH₂ groups [2,5]. Such downward frequency shifts may be attributed to the weakening of the N-H bonds resulting from the electron drain from the two N atoms on account of their coordination between two consecutive outer metal (M = Ni, Co or Cd) atoms [2,5]. The other notable feature is that the asymmetric and symmetric stretching vibrations of the NH₂ groups appear as two single sharp bands. There are no signs of splitting for these bands. The absence of splitting implies that the ligand molecule in the compounds behaves as a bridging ligand (bidentate coordination). Similar downward shifts have also been observed in related systems [2,5]. Based on the present spectral data, it is not possible to deduce the conformation of the danon molecules in the host framework.

Table 3. The vibrational frequencies (cm⁻¹) of 1, 9 -diaminononane in M-danon-Ni-G clathrates.

Assignment ^a	Danon in CCl ₄	Ni-Ni-Bz ^a	Ni-Ni	Ni-Ni-NB	Co-Ni-NB	Cd-Ni-NB
ν_a (NH ₂)	3361 vs	3356 vs	3366 vs	3347	3343 m	3357 m
ν_s (NH ₂)	3325 vs	3296 vs	3298 s	3293	3292 m	3293 m
ν_a (CH ₂)	2926 vs	2922 vs	2921 vs	2922 vs	2923 vs	2931 vs
ν_s (CH ₂)	2856 vs	2852 vs	2851 vs	2853 vs	2853 vs	2853 vs

$\delta(\text{NH}_2)$	1581 vs	1587 vs	1586 s	1588 s	1587 m	1587 s
$\delta(\text{CH}_2)$	1489 vs	1472 vs	-	1464s	1505 m	-
$\delta(\text{CH}_2)$	1472 vs	1460 s	1465 s	1466 s	1464 vs	1467 vs
$\rho_w(\text{CH}_2)$	1390 s	-	1396 w	1377 s	1394w	1377 s
$\rho_w(\text{CH}_2)$		1377 s	1362 w	1372w	1377 s	1377s
$\rho_t(\text{CH}_2)$	1313 m	1307 m	1306 w	1316 s	1317 m	1317m
$\rho_t(\text{NH}_2)$	1225 w	1205 w		1243 m	1222 w	-
$\gamma(\text{CN})$	1097 vw	1106 vw		1107 s	1107 m	1106 m
$\gamma(\text{CN})$	1070 w	1067 s		1060 s	1070 s	1069 m
$\rho_w(\text{NH}_2)$		1014 w	1014 s	1021 s	1020 m	1041 m
$\rho_t(\text{CH}_2)$	931 m	964 vw		939 m	964 m	960 m
$\rho_t(\text{CH}_2)$	877 m	854 m		850 s	850 m	851 s
$\rho_t(\text{CH}_2)$	721 m	723 s	724 m	714 s	710 s	710 vs
$\delta(\text{skel})$	576 m	575 m	580 s	576 vs		

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189 However, some implications may be deduced from the spectral features of the danon
190 molecules in the clathrates that are found to be similar, suggesting similar conformations.
191 The compositions of the present compounds suggest that one of the two cavities may be
192 occupied by the skeletal carbon-chain instead of a guest molecule in such a way that the
193 bridging diamino ligand takes an appropriate skeletal conformation. The symmetric and
194 asymmetric C-H stretching vibrations occur in the expected ranges of 2853 cm^{-1} and 2922--
195 2931 cm^{-1} respectively. These values correlate well with the reported values for 1,9-
196 diaminononane [2,16] and 1,6-diaminohexane [10]. The IR vibrational band of $\rho_w(\text{NH}_2)$ mode
197 in all clathrates is found to be shifted to higher frequencies than that of danon molecule in
198 CCl_4 . Similar positive shifts have been observed for Hofmann-type clathrates [16,17]. This
199 shift was explained in terms of the above weak hydrogen bonding. All the vibrations of the
200 ligand molecule are observed at comparable regions for the host and the clathrate **1** (Figure
201 2) indicating the absence of any significant changes in the host structure on insertion of the
202 guest molecule.

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3.3. $\text{Ni}(\text{CN})_4$ group vibrations

205 The assigned wavenumbers for $\text{Ni}(\text{CN})_4$ group in compounds **1-3** are given in Table 4. For a moiety
206 having D_{4h} symmetry, only 4 fundamental vibrations are expected in the IR spectrum above 400 cm^{-1}
207 [2,3,7-10] which are deduced and assigned for the present clathrates. The absence of splitting of the
208 E_u mode implies that, the slight distortion from tetragonal symmetry seems to be too small to have any
209 effect on the vibrational spectra [8]. The IR band $\nu_8(\text{CN})$ of the cyanide moiety in the present
210 clathrates is observed in the range of $2148\text{--}2163\text{ cm}^{-1}$ for the cobalt, cadmium and nickel analogues.
211 Similar results have also been noticed for $\text{Ni}(\text{danon})\text{Ni}(\text{CN})_4\cdot\text{G}$ (G = benzene, naphthalene, anthracene,
212 phenanthrene) [2] as well as $\text{M}(\text{dahxn})\text{Ni}(\text{CN})_4\cdot\text{G}$ (G = chlorobenzene, o-, m- and p-dichlorobenzene;
213 M = Co, Ni, Cd) [10]. As the characteristic frequencies of the $\text{Ni}(\text{CN})_4^{2-}$ unit are similar to those of the

Hofmann-type clathrates [2,3,10,18,19], it is assumed that the coordination about the Ni atom is square planar and $(M-Ni(CN)_4)_\infty$ (M = Co, Ni or Cd) layers have been preserved.

Table 4. The vibrational frequencies (cm^{-1}) of $Ni(CN)_4$ group in M-danon-Ni-G clathrates.

Assignment ^a	Na ₂ Ni(CN) ₄ ^a	Ni-Ni-Nap ^b	Ni-Ni	Ni-Ni-NB	Co-Ni-NB	Cd-Ni-NB
$\nu_8(CN)$ Eu	2132 vs	2166 vs	2166 vs	2163 s	2158 s	2148
Hot band	2128 w	-	-	2121 sh	2114 m	
$\nu_9(NiC)$ Eu	543 m	-	-	471 w	494	557
$\nu_9(NiC)$ Eu			-	438 s	464 m	
$\pi(NiC)$ A _{2u}	448 w	476 vw		416 m	438 vs	
$\delta(NiCN)$ Eu	433 s	440 vs	439 vs	408 m	414	

a – Taken from reference [14]; b -Ni(danon)Ni(CN)₄.Naphthalene [2]

All the vibrational modes of $Ni(CN)_4^{2-}$ groups in the compounds studied are shifted to higher frequency region relative to isolated $Ni(CN)_4^{2-}$ units [14]. $\nu_8(CN)$ mode shows about 16-33 cm^{-1} upward shift similar to that observed in Hofmann-type clathrates[2,3,8,18] in which both ends of cyanide group are bonded to transition metals and explained due to the mechanical coupling of the internal modes of $Ni(CN)_4^{2-}$ with the metal-MNC vibrations [3,18]. The $\nu(CN)$ frequencies in the present clathrates are found to be in the order, Cd-Ni-G < Co-Ni-G < Ni-Ni-G. A similar variation has been observed in the IR spectra of other Hofmann- α,ω -diaminoalkane-type clathrates [2,3,10] and explained to be due to the decreasing ionic radii, increasing electronegativity and second ionization potential of outer metal ions [20,21]. The C-N stretching frequency of the host, Ni(danon)Ni(CN)₄ occurs at 2166 cm^{-1} . However the corresponding peak for the clathrate Ni-Ni-An is observed at 2163 cm^{-1} . The downshift of 3 cm^{-1} corroborates the hydrogen bonding between $C\equiv N$ and the NO_2 group of guest nitrobenzene as deduced from the changes in the N-O vibrations.

3.4. Declathration by heating

The behaviour of nitrobenzene clathrates (1-3) is different in that, heating at 200°C for 4 hours in oven, leads to partial liberation of guest molecule which is apparent from the intensity of CHop deformation mode of nitrobenzene (Figure 2). Under similar conditions, our earlier aniline clathrates having the same host lattice, on heating loses all the characteristic peaks of guest aniline. Thus, nitrobenzene clathrates are more stable than other clathrates. This may be due to greater hydrogen bonding interaction as well as high boiling point of nitrobenzene. After heating and cooling, the guest sites which become vacant, may be occupied by moisture as evidenced by the peaks at 3630 and 3570 cm^{-1} due to weak hydrogen bonding of water with the host lattice.

4. CONCLUSION

In this chapter, IR spectra of three new tetracyanonickelate complexes with 1,9-diaminonone as ligand and three of their clathrates with guest nitrobenzene are presented. It is shown that they have similar structures and exhibit weak hydrogen bonding between the π -cloud of aromatic guest and the ligand of the host lattice which is observed in all clathrates. Nitrobenzene clathrates are more stable

247 than other clathrates. This may be due to greater hydrogen bonding interaction as well as high boiling
248 point of nitrobenzene.

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