



Inclusion Compounds Formed between Hofmann-(1,9-diaminononane)-type Host and Aromatic Guest

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Authors' contributions

This work was carried out in collaboration between all authors. Author GI designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors AT and RG managed the analyses of the study. All authors read and approved the final manuscript.

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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 pi-electron cloud of aromatic guest and the ligand of the host lattice which is observed in all clathrates. A second type of hydrogen bonding is present between the NO₂ 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-NB < Co-Ni-NB < Ni-Ni-NB 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 it's 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 lattices 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 NO₂ of nitrobenzene, pi cloud of the guest and the cyanide moieties.

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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. Hofmann-type clathrates exhibit such type of interactions, varying from charge transfer forces to weak hydrogen bondings [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 = divalent metal ion; G = aromatic guest molecule), a series of analogous clathrates of general formula, $M(diam)Ni(CN)_4 \cdot G$ ($diam$ = α, ω -diaminoalkane = $NH_2(CH_2)_nNH_2$) were developed [2,3]. The three-dimensional host lattices of such clathrates have been prepared from the two-dimensional lattice by replacing the unidentate by bidentate ligand in 2:1 ratio. The XRD study of $Cd(danon)Ni(CN)_4 \cdot 0.5o$ -xylene [4] reveals a typical model for the Hofmann-diam-type host structure as shown in Fig. 1. Although the IR spectra of $Ni(danon)$ -td-type clathrates have been reported [5], the only study available on Hofmann-danon-type clathrates concerns with the guest benzene, naphthalene, anthracene and 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.

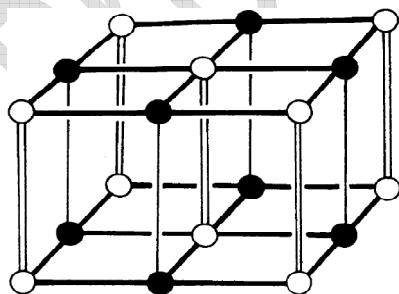


Fig. 1. The model for the Hofmann-diam-type host structure (open circle: 6-coordinate M, solid circle: square-planar Ni, open column: an ambidentate ligand, thick line: CN bridge and thin line: edge of cavity)

2. MATERIALS AND METHODS

2.1 Synthesis of $K_2[Ni(CN)_4]$

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 solution of nickel sulphate ($NiSO_4 \cdot 7H_2O$; 5.75 gm in 50 ml water = 20 mmol), a KCN solution (40 mmol; 2.60 gm in 50 ml water) was added with constant stirring. A white precipitate of $Ni(CN)_2$ formed was separated and dissolved by adding an excess of KCN solution (40 mmol). The resulting solution was filtered off, concentrated on a water bath and kept undisturbed. Colorless crystals of $K_2[Ni(CN)_4]$ appeared within a week. They were collected and dried in an air oven at 110°C for two hours. It was kept in a desiccator.

2.2 Synthesis of Host Complexes

Typically one mmol of $K_2Ni(CN)_4$ was dissolved in water (20 mL). To this solution, one mmol of the ligand and one mmol of the metal chloride, dissolved in ethanol (5 mL each), were added with constant stirring. The resultant solution was filtered off and kept undisturbed for slow evaporation. The powdery compounds, obtained in a week's time, were filtered off, washed with water and ethanol successively and dried in an air oven at 100°C. Then they were kept in a desiccator containing anhydrous solid calcium chloride. The complexes thus prepared were: $M(danon)Ni(CN)_4$ and abbreviated as $Ni-Ni$ (**1'**), $Co-Ni$ (**2'**) and $Cd-Ni$ (**3'**). Samples of the compounds were stable at atmospheric temperature and polycrystalline in nature.

2.3 Synthesis of the Clathrates by Solution Method

3 mmol of the guest and 1 mmol of danon contained in a solution of ethanol and 1 mmol of aqueous solution of $K_2Ni(CN)_4$ were added to a 1 mmol aqueous solution of MCl_2 ($M = Co, Ni$ or Cd) with stirring. The clathrate was filtered, washed with water and ethanol successively and kept in a desiccator containing saturated guest vapour. The clathrates obtained by the above procedure are:

Ni(danon)Ni(CN)₄.Nitrobenzene (**1**);
abbreviated as Ni-Ni-NB
Co(danon)Ni(CN)₄.Nitrobenzene (**2**);
abbreviated as Co-Ni-NB
Cd(danon)Ni(CN)₄.Nitrobenzene (**3**);
abbreviated as Cd-Ni-NB

2.4 Physical Measurements

The freshly prepared clathrate compounds were analyzed for C, H and N using the CHNS analyzer, Varian Micro cube and LECO CHNS-932 and the metals by atomic absorption spectra. The results are given in Table 1. The results indicate that the number of guest molecules in the present compounds is one as reported earlier [2,3,7-10]. FT-IR spectra were recorded between 4000-400 cm⁻¹ on a JASCO 400-FT-IR spectrometer with the resolution of 4 cm⁻¹. The spectrometer was calibrated using a standard polystyrene film. The samples were prepared as mulls in nujol placed between NaCl discs and as KBr discs. At ambient conditions, the samples decompose, and hence a fresh sample preserved under guest vapours was used.

3. RESULTS AND DISCUSSION

Due to the flexibility of the host frame-work with long diamine ligand, the number of guest molecules packed 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 is obvious from XRD study [4], that one of the two cavities is occupied by the skeletal carbon-chain with suitable conformation instead of a guest molecule as observed in Hofmann-daon-type clathrates [12].

3.1 Nitrobenzene Guest Vibrations

There are three distinct set 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 lattice. 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 Fig. 2. The IR spectra 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 show 1-7 cm⁻¹ shifts to higher frequencies compared to liquid nitrobenzene (793, 703, 676 cm⁻¹) in literature [13,14]. 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.

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 NH₂ of the ligand in the host structure. The corresponding mode of nitrobenzene in **1** shows no shift at 793 cm⁻¹ but the other modes of $\gamma(\text{CH})$ at 703 and 676 cm⁻¹ for the compounds **1-3** show (1-7 cm⁻¹) shifts to higher frequencies. But this shift is small compared to that of benzene in benzene clathrates (11-18 cm⁻¹) [2,8]. It may probably be due to the presence of a weak hydrogen bonding between the π -electron cloud of nitrobenzene 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. Among the three compounds, **1-3**, the shift is maximum in **2** and **3**. The above mentioned hydrogen bonding is also evidenced by the red shift in $\nu_a(\text{CH})$ and $\nu_s(\text{CH})$ compared to free nitrobenzene values of 3100 and 3080 cm⁻¹ respectively and also in ν_{ring} (1606 cm⁻¹). Also, $\gamma(\text{CH})_{\text{op}}$ modes of clathrates **2** and **3** show blue shift (upto 7 cm⁻¹) than that of liquid NB similar to observations made in **1**. Further evidence comes from the appearance of new peaks which are noted in Table 2. These spectral features of the clathrates **2** and **3** indicate that they may have similar structures as that of **1**.

3.2 Vibrations of 1,9-diaminononane

The vibrational frequencies and assignments of the fundamental bands of the ligand (danon) in the compounds under study are given in Table 3 along with that for danon in CCl₄ for comparison. The peaks observed for the clathrates, **1-3**, in the range 3343-3357 cm⁻¹ and 3292-3293 cm⁻¹, assigned to the NH₂ asymmetric and symmetric stretching frequencies of danon, are lower than that for free ligand in CCl₄ solution (3361 cm⁻¹

and 3325 cm^{-1} respectively) [2]. The values are characteristic of coordinated NH_2 groups [2,5]. Such red shifts may be attributed to the weakening of the N-H bonds, due to the coordination of N atoms between two consecutive outer metal ($M = \text{Ni}, \text{Co}$ or Cd) atoms [2,5]. The asymmetric and symmetric stretching vibrations of the NH_2 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. Similar downward shifts are also observed in related systems [2,5].

Similar spectral features of the danon molecule in the clathrates, suggest similar conformations too. The compositions of the present compounds suggest that one of the two cavities may be

occupied by the skeletal carbon-chain instead of a guest molecule in such a way that the bridging diamino ligand takes an appropriate skeletal conformation. The symmetric and asymmetric C-H stretching vibrations occur in the expected ranges of 2853 cm^{-1} and $2922\text{-}2931\text{ cm}^{-1}$ respectively. These values correlate well with the reported values for 1,9-diaminononane [2,15]. The IR vibrational band of $\rho_w(\text{NH}_2)$ mode in all clathrates is found to be blue shifted than that of danon molecule in CCl_4 . Similar blue shift have been observed for Hofmann-type clathrates [15,16] and was attributed to the weak hydrogen bonding between ligand NH and pi-cloud of guest. All the vibrations of the ligand molecule are observed at comparable regions for the host and the clathrate (Table 3), indicating the absence of any significant changes in the host structure on insertion of the guest molecule.

Table 1. Results of elemental analysis (found % /calculated %) for 1-3

Compound	C %	H%	N%	Ni%	%
$\text{Ni}(\text{C}_9\text{H}_{22}\text{N}_2)\text{Ni}(\text{CN})_4\cdot\text{C}_6\text{H}_5\text{NO}_2$ (1)	45.13/45.38	5.26/5.37	19.32/19.51	23.41/23.36	
$\text{Co}(\text{C}_9\text{H}_{22}\text{N}_2)\text{Ni}(\text{CN})_4\cdot\text{C}_6\text{H}_5\text{NO}_2$ (2)	45.17/45.36	5.45/5.37	19.28/19.50	11.59/11.68	Co =11.65/11.72
$\text{Cd}(\text{C}_9\text{H}_{22}\text{N}_2)\text{Ni}(\text{CN})_4\cdot\text{C}_6\text{H}_5\text{NO}_2$ (3)	40.79/41.00	4.71/4.86	17.46/17.62	10.42/10.56	Cd =20.23/20.22

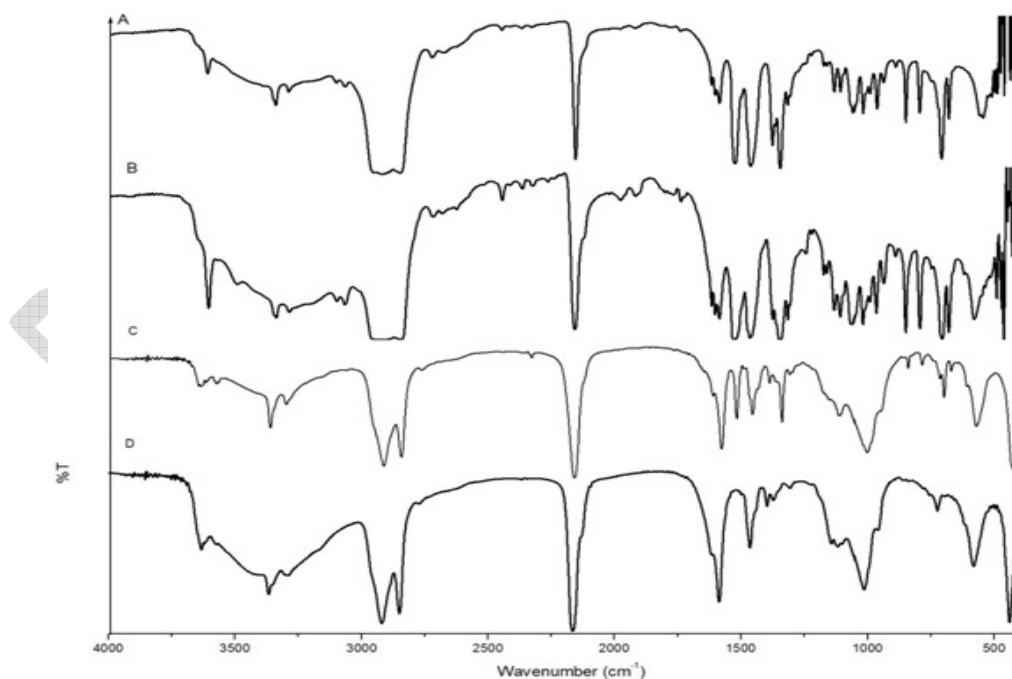


Fig. 2. FT-IR spectra of (A) clathrate Co-Ni-NBz (2) in nujol; (B) clathrate Ni-Ni-NBz (1) in nujol; (C) heated (1) in KBr and (D) the host Ni-Ni (1') in KBr

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)
v _a CH	3100 m	3106 s	3106 m	3105 w
v _s CH	3080 m	3076 s	3071 m	3071 w
v CC	1606 m	1605 vs	1604 m	1603 m
v _a (N=O ₂)	1523 s	1530 s	1524 s	1523 vs
v _s (N=O ₂)	1347 s	1347 s	1346 vs	1346 s
v _s (N=O ₂)	1108 m	1107 s	1107 m	1106 m
v _s (N=O ₂)	1021 m	1020 w	1020 m	1018 m
v C-N	852 s	850 s	850 m	851 s
γ CHo.p	793 s	793 s	796 m	797 s
γ CHo.p	703 s	704 s	710 s	710 vs
γ CHo.p	676 s	680 s	681 m	681 s

^aTaken from reference[13]**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
v _a (NH ₂)	3361 vs	3356 vs	3366 vs	3347	3343 m	3357 m
v _s (NH ₂)	3325 vs	3296 vs	3298 s	3293	3292 m	3293 m
v _a (CH ₂)	2926 vs	2922 vs	2921 vs	2922 vs	2923 vs	2931 vs
v _s (CH ₂)	2856 vs	2852 vs	2851 vs	2853 vs	2853 vs	2853 vs
δ(NH ₂)	1581 vs	1587 vs	1586 s	1588 s	1587 m	1587 s
δ(CH ₂)	1489 vs	1472 vs	-	1464s	1505 m	-
δ(CH ₂)	1472 vs	1460 s	1465 s	1466 s	1464 vs	1467 vs
ρ _w (CH ₂)	1390 s	-	1396 w	1377 s	1394w	1377 s
ρ _w (CH ₂)	-	1377 s	1362 w	1372w	1377 s	1377s
ρ _t (CH ₂)	1313 m	1307 m	1306 w	1316 s	1317 m	1317m
ρ _t (NH ₂)	1225 w	1205 w	-	1243 m	1222 w	-
γ(CN)	1097 vw	1106 vw	-	1107 s	1107 m	1106 m
γ(CN)	1070 w	1067 s	-	1060 s	1070 s	1069 m
ρ _w (NH ₂)	-	1014 w	1014 s	1021 s	1020 m	1041 m
ρ _r (CH ₂)	931 m	964 vw	-	939 m	964 m	960 m
ρ _r (CH ₂)	877 m	854 m	-	850 s	850 m	851 s
ρ _r (CH ₂)	721 m	723 s	724 m	714 s	710 s	710 vs
δ(skel)	576 m	575 m	580 s	576 vs	-	-

^a[2]

3.3 Cyanide Lattice Vibrations

The assigned wavenumbers for metal cyanide group in compounds **1-3** are given in Table 4. Since Ni(CN)₄ has square planar geometry with D_{4h} point group, it exhibits only 4 vibrations which are deduced and assigned for the present clathrates. The IR band u(CN) of the cyanide moiety in the present clathrates is observed in the range of 2148-2163 cm⁻¹ for the cobalt, cadmium and nickel analogues. Similar results have been noticed for Ni(danon)Ni(CN)₄.G [2] in the range (2148-2166 cm⁻¹). u(CN) mode shows about 16-33 cm⁻¹ blue shift than that of isolated Ni(CN)₄²⁻ units (2132 cm⁻¹) [13]. This is similar to that observed in Hofmann-type clathrates [2,3,8,17,18] in which cyanide group is bridged between metals (Ni-CN-M). The presence of

single u(CN) peak implies that all the four cyanides are bridging in nature. The u(CN) frequencies in the present clathrates are found to be in the order, Cd-Ni-NB < Co-Ni-NB < Ni-Ni-NB. A similar variation has been observed for other Hofmann-α,ω-diaminoalkane-type clathrates [2,3,10] and explained to be due to the decreasing ionic radius, increasing electronegativity and second ionization potential of outer metal ions [19,20]. The u(CN) 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≡N and the NO₂ group of guest nitrobenzene as deduced from the changes in the N-O vibrations.

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
v(CN)	2132 vs	2166 vs	2166 vs	2163 s	2158 s	2148
Hot band	2128 w	-	-	2121 sh	2114 m	
v(NiC)	543 m	-	-	471 w	494	557
v(NiC)				438 s	464 m	
π(NiC)	448 w	476 vw		416 m	438 vs	
δ(NiCN)	433 s	440 vs	439 vs	408 m	414	

a – Taken from reference [13]; b -Ni(danon)Ni(CN)₄Naphthalene [2]

u(CN) mode shows about 16-33 cm⁻¹ blue shift than that of isolated Ni(CN)₄²⁻ units (2132 cm⁻¹) [14]. This is similar to that observed in Hofmann-type clathrates [2,3,8,17] in which cyanide group is bridged between metals (Ni-CN-M). The presence of single u(CN) peak implies that all the four cyanides are bridging in nature. The u(CN) frequencies in the present clathrates are found to be in the order, Cd-Ni-NB < Co-Ni-NB < Ni-Ni-NB. A similar variation has been observed for other Hofmann-α,ω-diaminoalkane-type clathrates [2,3,10] and explained to be due to the decreasing ionic radius, increasing electronegativity and second ionization potential of outer metal ions [19,20]. The u(CN) 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≡N and the NO₂ group of guest nitrobenzene as deduced from the changes in the N-O vibrations.

3.4 Declathration by Heating

The thermal behaviour of nitrobenzene clathrates (1-3) is different 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 (Fig. 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 paper, IR spectra of three new 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 the clathrates are formed through weak hydrogen bonding between guest and host lattice. 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.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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