

Comparing of the host–guest interaction in the Hofmann-1, 10-diaminododecane and Hofmann-1,12-diaminododecane-type clathrates

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Abstract $M(1,12\text{-diaminododecane})Ni(CN)_4 \cdot G$ ($M = Co, Ni$ or Cd ; $G =$ chlorobenzene; 1,2-; 1,3- or 1,4- dichlorobenzene) clathrates were prepared in powder form for the first time and their infrared spectra were reported and then compared with $M(1,10\text{-diaminododecane})Ni(CN)_4 \cdot 1,5G$ ($M = Co, Ni$ or Cd ; $G =$ chlorobenzene; 1,2-; 1,3- or 1,4-dichlorobenzene) clathrates. The spectral results suggest that the characteristic $\nu(CN)$ and $\delta(NiCN)$ frequencies are found to be similar to those known for the Hofmann type compounds, in that prepared compounds are similar in structure to this type compounds and their structures consist of polymeric layers $[M-Ni(CN)_4]_{\infty}$ with the 1,12-diaminododecane molecule bound to the metal atom (M). Also, the results suggest that the ligand molecule with 10 to 12 of chain length have no effect on vibrational bands of the guest molecules in the similar Hofmann-diam-type clathrates. The normal mode frequencies and corresponding vibrational assignments of chlorobenzene and 1,2-; 1,3- or 1,4-dichlorobenzene in the ground state were calculated by DFT/B3LYP level of theory using the 6-311G(d, p) basis set in Gauss-view. In addition, these theoretical results were compared to the experimental results for the vibrational modes of host molecules.

Keywords Infrared · Spectroscopy · Clathrates · Benzene derivative

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Introduction

In our previous work [1] we reported that the structure of $M(dadn)Ni(CN)_4 \cdot 1,5G$ ($M = Co, Ni$ or Cd ; $dadn =$ 1,10-diaminododecane; $G =$ chlorobenzene; 1,2-; 1,3- or 1,4-dichlorobenzene) (abbr. $M\text{-}dadn\text{-}Ni\text{-}G$) are similar to those found in Hofmann-diam-type clathrates given with a general formula $M(\alpha,\omega\text{-diaminoalkane})Ni(CN)_4 \cdot nG$, where M is transition metals such as Co, Ni or Cd ; n is the number of G (guest) molecules depending on the bulkiness of the ligands [2]. The Hofmann-type host frame work is formed from infinite $[M-Ni(CN)_4]_{\infty}$ layers with four planar coordination around Ni atom [2, 4–6]. The structure provides an α -type cavity (rectangular box) for the guest molecules [4–6]. When the ligand 1,8-diaminooctane exchange with 1,10-diaminododecane and 1,12-diaminododecane (abbr. $daddn$) ligand, the guest molecules enter the α -type cavity as seen in the network in Fig. 1 [3]. The size-dependence is quantitatively estimated by the ligand chain length, which is the volume ratio of a guest molecule to a host cavity. Each of the host frameworks has its own range of the values. The host frameworks are selected by host–guest interactions through weak hydrogen bonds. The weak hydrogen bonds play an important role for various selective inclusion processes. The host frameworks are dynamically exchangeable due to length of ligand chain, resulting in intercalation of the cavities. These static and dynamic structures of the frameworks demonstrate great potential of inclusion compounds as functional materials.

In the present work, twelve new $M(daddn)Ni(CN)_4 \cdot G$ ($M = Co, Ni$ or Cd ; $G =$ chlorobenzene; 1,2-; 1,3- or 1,4-dichlorobenzene) (abbr. $M\text{-}daddn\text{-}Ni\text{-}G$) clathrates were prepared in powder form and their infrared spectra were reported for the first time.

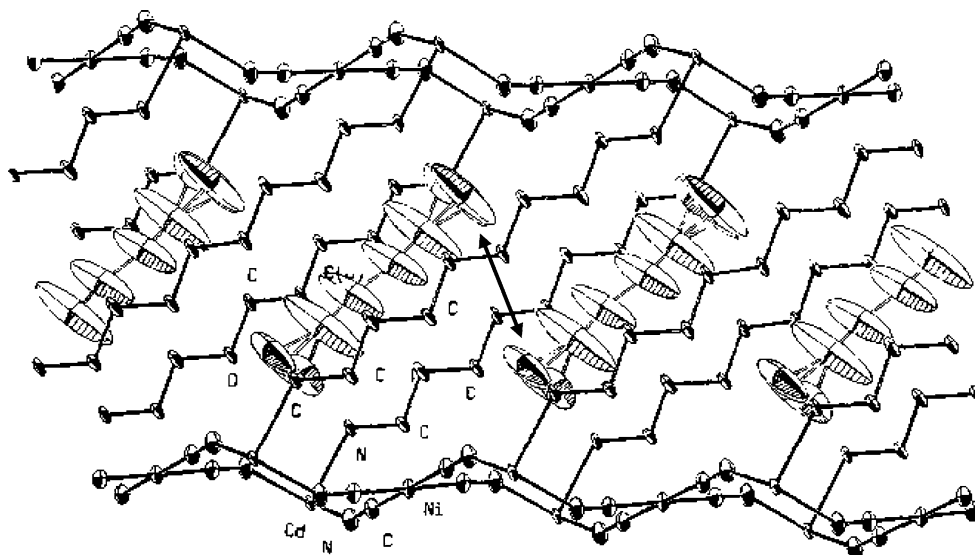


Fig. 1 ORTEP view of (1,8-diaminooctane)cadmium(II)tetra-cyano-nickelate(II)-(1-hexanol) [1/1]. Those of the hydrogen atoms are omitted [3]. (The number of carbon in the chain structured

molecules used as ligand can be increased to 10 to 12. The guest molecules in the figure can exchange with a guest molecules to be used)

Experimental

The compounds $M(\text{daddn})\text{Ni}(\text{CN})_4 \cdot G$ ($M = \text{Co}, \text{Ni}$ or Cd ; $G = \text{chlorobenzene}; 1,2\text{-}; 1,3$ or $1,4\text{-dichlorobenzene}$) were prepared by adding slightly more than 1 mmol of *daddn* to a solution containing 1 mmol of $\text{K}_2\text{Ni}(\text{CN})_4$, 1 mmol of MCl_2 ($M = \text{Co}, \text{Ni}$ or Cd), 20 mmol water and 20 mmol ethanol, saturated with the guest molecules. The precipitate was filtered, washed with water, ethanol and ether, successively, and kept in a desiccators containing molecular sieves and saturated guest vapour. IR spectra of the clathrate compounds were recorded in the range of $4,000\text{--}400\text{ cm}^{-1}$

on a MATTSON 1000 FTIR spectrometer, which was calibrated using an indene/camphor/cyclohexane standard solution.

The samples were prepared as mulls in nujol and hexachlorobutadiene between CsI windows and as KBr discs.

The calculated vibrational frequencies and experimental values are presented in Tables 3, 4, 5, and 6. The infrared spectrum of $\text{Co}(\text{daddn})\text{Ni}(\text{CN})_4 \cdot \text{ClBz}$ clathrate is given in Fig. 2.

The freshly prepared compounds were analyzed for C, H and N by a LECO CHNS-932 analyzer. The results are as follows (found %/calculated %) :

Fig. 2 IR spectrum of $\text{Co}(1,12\text{-diaminododecane})\text{Ni}(\text{CN})_4 \cdot \text{ClBz}$ clathrate (mulls in nujol and hexachlorobutadiene between CsI windows)

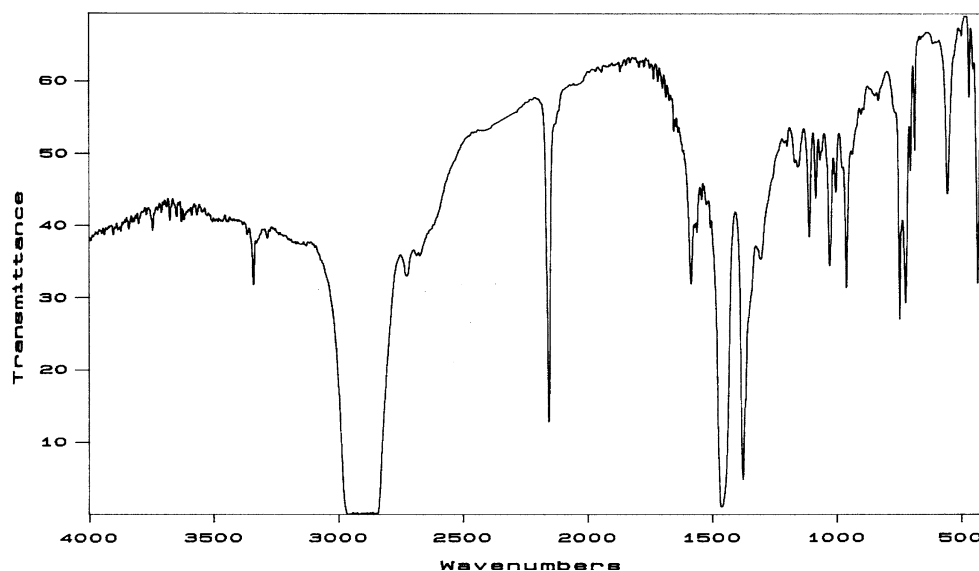


Table 1 The vibrational wavenumbers (cm⁻¹) of 1,12-diaminododecane in the M-daddn-Ni-G (M = Co, Ni or Cd; G = chlorobenzene; 1,2-dichlorobenzene; 1,3-dichlorobenzene, 1,4-dichlorobenzene)^a

Assignment ^b	daddn in CCl ₄ ^c	Cd-Ni-daddn-CIBz ^d	Co-Ni-CIBz	Ni-Ni-CIBz	Cd-Ni-1,2CIBz	Co-Ni-1,3CIBz	Ni-Ni-1,3CIBz	Cd-Ni-1,3CIBz	Co-Ni-1,4CIBz	Ni-Ni-1,4CIBz	Cd-Ni-1,4CIBz		
$\nu_a(\text{NH}_2)$	3,364 m	3,350 s	3,340 m	3,342 m	3,342 m	3,341 m	3,343 m	3,343 m	3,343 m	3,347 m	3,345 m	3,346 m	3,346 m
$\nu_s(\text{NH}_2)$	3,330 s	329 m	3,284 m	3,285 m	3,284 m	3,286 m	3,286 m	3,287 m	3,288 m	3,290 m	3,290 m	3,292 m	3,292 m
$\nu_a(\text{CH}_2)$	2,920 vs	2,919 vs	2,923 vs	2,920 vs	2,919 vs	2,922 vs	2,923 vs	2,923 vs	2,924 vs	2,923 vs	2,923 vs	2,921 vs	2,922 vs
$\nu_s(\text{CH}_2)$	2,849 vs	2,850 vs	2,851 vs	2,850 vs	2,850 vs	2,851 vs	2,851 vs	2,850 vs	2,851 vs	2,851 vs	2,851 vs	2,851 vs	2,850 vs
$\delta(\text{NH}_2)$	1,605 w,sh	-	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.
$\delta(\text{NH}_2)$	1,578 vs	1,583 vs	1,584 s	1,585 s	1,584 s	1,586 s	1,587 s	1,586 s	1,586 vs	1,588 vs	1,586 vs	1,586 vs	1,588 vs
$\delta(\text{CH}_2)$	1,490 m,sh	-	1,506 w	1,506 w	1,505 w	1,497 m	1,496 m	1,495 m	1,497 m	1,497 m	1,497 m	1,498 m	1,496 m
$\delta(\text{CH}_2)$	1,464 s	1,470 s	1,469 m	1,470 m	1,469 m	1,466 m	1,467 m	1,467 m	1,468 m	1,468 m	1,470 m	1,469 m	1,468 m
$\delta(\text{CH}_2)$	1,437 w	1,445 w	1,436 vw	1,431 vw	1,435 vw	n.o.	n.o.	n.o.	1,440 w	1,437 w	1,438 w	1,439 w	1,438 w
$\rho_w(\text{CH}_2)$	1,393 w	1,381 vw	1,397 vw	1,398 vw	1,400 vw	1,393 w	1,393 w	1,396 w	1,396 w	1,396 w	1,393 w	1,398 w	1,396 w
$\rho_w(\text{CH}_2)$	1,367 w	1,355 vw	1,380 vw	1,381 vw	1,377 vw	1,378 vw	1,381 vw	1,383 vw	1,384 vw	1,383 vw	1,383 vw	1,383 vw	1,385 vw
$\rho_l(\text{CH}_2)$	1,346 w	1,338 vw	1,355 vw	1,359 vw	1,360 vw	1,357 vw	1,357 vw	1,357 vw	1,359 vw	1,356 vw	1,360 vw	1,354 vw	1,357 vw
$\rho_l(\text{CH}_2)$	1,321 vw	-	1,341vw	1,341vw	1,340 vw	1,341 vw	1,341 vw	1,343 vw	1,342 vw	1,343 vw	1,344 vw	1,342 vw	1,343 vw
$\rho_l(\text{NH}_2)$	1,302 w	1,306 w	1,301 vw	1,307 vw	1,305 vw	1,307 w	1,306 w	1,308 w	1,306 w	1,308 w	1,304 w	1,308 w	1,307 w
$\nu(\text{CN})$	1,098 w	1,101 s	1,111 m	1,111 m	1,103 m	1,107 m	1,109 m	1,099 m	1,110 m	1,111 m	1,105 m	1,108 m	1,104 m
$\nu(\text{CN})$	1,065 s	-	n.o.	n.o.	n.o.	1,072 vw	1,072 vw	n.o.	n.o.	n.o.	n.o.	1,088 vw	1,081 vw
$\nu(\text{CN})$	1,061 s	1,057 m,sh	1,061 w	1,060 w	1,058 w	1,058 w	1,058 w	1,057 w	1,060 w	1,061 w	1,060 w	1,050 w	1,056 w
$\nu(\text{CC})$	1,020 w	-	1,028 s	1,032 s	1,023 s	1,023 s	1,029 s,sh	1,020 s	1,027 s	1,030 s	1,022 s	1,028 s	1,027 s
$\rho_w(\text{NH}_2)$	1,004 m	1,020 w	1,003 w	1,011 w	1,001 vw	n.o.	n.o.	n.o.	1,007 vw	1,006 vw	1,007 vw	1,005 vw	1,005 vw
$\rho_l(\text{CH}_2)$	-	1,001 s	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.
$\rho_w(\text{NH}_2)$	982 s	-	961 m	965 m	957 m	978 w	978 w,sh	979 w	981 w	981 w	981 w	978 w	981 w
$\rho_w(\text{NH}_2)$	934 w	-	937 vw	938 vw	937 vw	940 vw	939 vw	940 vw	937 vw	934 vw	939 vw	942 vw	935 vw
$\rho_w(\text{NH}_2)$	913 s	-	920 vw	919 vw	919 vw	918 vw,sh	925 vw,sh	918 vw,sh	920 vw	918 vw	918 vw	918 vw	922 vw
$\rho_l(\text{CH}_2)$	897 s	-	897 vw	897 vw	897 vw	893 vw	895 vw	893 vw	893 vw	893 vw	893 vw	892 vw	894 vw
$\rho_l(\text{CH}_2)$	819 w	-	818 vw	822 w,sh	816 vw	818 vw	818 vw	818 vw	818 vw	831 vw	834 vw	827 vw	835 vw
$\rho_l(\text{CH}_2)$	731 m	-	739 vw	738 vw	740 vw	740 vw	740 vw	738 vw	n.o.	n.o.	n.o.	738 vw	741 vw
$\rho_l(\text{CH}_2)$	722 s	736 w	724 m	724 m	724 m	723 m	723 m	723 m	726 m	725 m	722 m	727 m	722 m
$\delta(\text{skeletal})$	480 w	535 m	555 m	577 m	535 m	551 m	573 m	526 m	553 m	575 m	526 m	548 m	532 m

^a ν very, s strong, m medium, w weak, sh shoulder, $n.o.$ not observed. ^b Taken from Ref [9]. ^c Taken from Ref [6]. ^d Taken from Ref [1]

Co(1,12-diaminododecane)Ni(CN)₄.ClBz: C = 49.52/49.42, H = 6.35/6.22, N = 15.87/15.72;
 Co(1,12-diaminododecane)Ni(CN)₄.1,2ClBz:
 C = 47.02/46.93, H = 5.89/5.67, N = 14.96/14.77;
 Ni(1,12-diaminododecane)Ni(CN)₄.ClBz: C = 49.77/49.45, H = 6.51/6.22, N = 16.01/15.73;
 Ni(1,12-diaminododecane)Ni(CN)₄.1,2ClBz:
 C = 46.71/46.45, H = 5.99/5.68, N = 15.13/14.78;
 Cd(1,12-diaminododecane)Ni(CN)₄.ClBz: C = 45.72/44.93, H = 5.95/5.66, N = 14.43/14.29;
 Cd(1,12-diaminododecane)Ni(CN)₄.1,2ClBz:
 C = 43.27/42.45, H = 5.64/5.18, N = 13.66/13.50.

Calculations

The vibrational frequencies of the chlorobenzene and 1,2-, 1,3- or 1,4-dichlorobenzene molecules in the ground state are calculated by using Gauss-View molecular visualization program [7] and Gaussian 03 program package on the personal computer [8], B3LYP with the 6-311G(d,p) basis set, and scaled by 0.9668. These calculated mode frequencies were compared to the infrared spectrum of molecules, and given in Table 3, 4, 5, and 6. It is observed that the calculated and measured vibrational frequencies are in good agreement.

Results and discussion

The infrared (IR) spectra of the compounds M-daddn-Ni-G (M = Co, Ni or Cd; G = chlorobenzene; 1,2-, 1,3- or 1,4-dichlorobenzene) and M-dadn-Ni-G (M = Co, Ni or Cd; G = chlorobenzene; 1,2-, 1,3- or 1,4-dichlorobenzene) [1] are very similar. The similarities between the IR spectral features of the compounds suggest that they have also similar structural features. These in turn suggest that the degrees of the interactions of the guest molecules, the *daddn* [1] and *daddn* ligand and the Ni(CN)₄ species with their surrounding are almost the same for each compound [9]. It will be most convenient to divide the infrared vibrations into three groups arising from the ligands, the Ni(CN)₄ units and the guest molecule moieties, respectively. The infrared wavenumbers of the bands in the spectra of these species are tabulated in Tables 1, 2, 3, 4, 5, and 6, respectively, together with some relevant spectral data for comparison.

The assignments and the wavenumbers of the vibrational bands of the *daddn* molecule are given in Table 1 together with the spectral data for the *daddn* molecule in the liquid phase and in CCl₄ solution. Some vibration bands of *daddn* show shifts up or down when compared to the same vibrations in the pure ligands. These shifts can be

Table 2 The vibrational wavenumbers (cm⁻¹) of Ni(CN)₄ group in the M-daddn-Ni-G (M = Co, Ni, or Cd; G = chlorobenzene; 1,2-; 1,3- or 1,4-dichlorobenzene) clathrates^a

Assignment ^b	Na ₂ Ni(CN) ₄ ^b	Cd-Ni-dadn-ClBz ^c	Co-Ni-ClBz	Ni-Ni-ClBz	Cd-Ni-dadn-1,2ClBz ^c	Co-Ni-1,2ClBz ^c	Ni-Ni-1,2ClBz	Cd-Ni-1,2ClBz	Cd-Ni-1,4ClBz
$\nu_8(\text{CN})_4, E_u$	2132, 2128	2,148 vs	2,156 vs	2,165 vs	2,149 vs	2,157 vs	2,163 vs	2,149 vs	
Hot band ?	-	2,128 vw,sh	n.o.	n.o.	2,129 vw,sh	n.o.	n.o.	n.o.	
$\nu_9(\text{NiC}), E_u$	543	498 vw	498 vw	500 vw	502 vw	496 vw	497 vw	491 vw	
$\pi(\text{NiC}), A_{2u}$	448	445 vw	452 vw	455 vw	447 vw	452 vw	455 vw	446 vw	
$\delta(\text{NiCN}), E_u$	433, 421	424 vs	434 vs	438 vs	424 vs	435 vs	438 vs	423 vs	
Assignment ^b	Na ₂ Ni(CN) ₄ ^b	Cd-Ni-dadn-1,3ClBz ^c	Co-Ni-1,3ClBz	Ni-Ni-1,3ClBz	Cd-Ni-dadn-1,4ClBz ^c	Co-Ni-1,4ClBz ^c	Ni-Ni-1,4ClBz	Cd-Ni-1,4ClBz	
$\nu_8(\text{CN})_4, E_u$	2132, 2128	2,148 vs	2,157 vs	2,161 vs	2,147 vs	2,156 vs	2,162 vs	2,147 vs	
Hot band ?	-	2,122 vw,sh	2,126 w,sh	n.o.	2,124 w,sh	n.o.	n.o.	2,124 w,sh	
$\nu_9(\text{NiC}), E_u$	543	522 vw	526 vw	526 vw	522 vw,sh	528 vw	529 vw	523 vw	
$\pi(\text{NiC}), A_{2u}$	448	434 vw	452 vw	446 vw	445 vw	453 vw	455 vw	443 vw	
$\delta(\text{NiCN}), E_u$	433, 421	424 vs	435 vs	436 vs	422 vs	434 vs	438 vs	424 vs	

^a v very, s strong, m medium, w weak, sh shoulder, n.o. not observed, ^b Taken from Ref [11], ^c Taken from Ref [1]

explained by the consecutive inductive effect [10]. Similar shifts were observed in other Hofmann-type clathrates [10]. The NH_2 stretching frequencies, which are lower than the corresponding values of free *dadn* [1] and *daddn* molecules, show that the ligand molecules are bound directly to metal M (M = Co, Ni or Cd). Based on the present data it is not possible to give an account of the conformation of the *dadn* [1] and *daddn* ligands in our compounds.

The bands of the $\text{Ni}(\text{CN})_4$ ion in the compounds were assigned on the basis of the work of McCullough et al. who presented vibrational data for $\text{Ni}(\text{CN})_4^{2-}$ ion in $\text{Na}_2\text{Ni}(\text{CN})_4$ [11]. The assigned wavenumbers for $\text{Ni}(\text{CN})_4$ groups in our compounds are given in Table 2, together with the vibrational wavenumbers of $\text{Na}_2\text{Ni}(\text{CN})_4$. If the unit cell has the D_{4h} symmetry, only four fundamental vibrations are expected in the infrared spectrum above 400 cm^{-1} [12]. Four fundamental bands are assigned in the infrared spectra of compounds (Table 2). Therefore, since no splitting of the infrared E_u mode occurs, the slight distortion from tetragonal symmetry seems to be too small to have any effect on the vibrational spectra. The characteristic frequencies of the $\text{Ni}(\text{CN})_4$ group suggest that $[\text{Cd}-\text{Ni}(\text{CN})_4]_\infty$ layers have been preserved. The vibrational frequencies of the $\text{Ni}(\text{CN})_4$ group in the compounds studied appear to be shifted relative to isolated $\text{Ni}(\text{CN})_4$ units. Such

frequency shifts have been observed for other Hofmann-type clathrates and complexes [13, 14], in which both ends of the CN group are bonded to transition metals and explained to be the mechanical coupling of the internal modes of $\text{Ni}(\text{CN})_4$ with the metal (M–NC) vibrations [10, 12].

The assignment and the wavenumbers of the bands arising from the guest molecules chlorobenzene (vapour phase, in-plane vibrations [15], out-of-plane vibration [16]); 1,2-; 1,3- and 1,4-chlorobenzene (in solution in CCl_4 and CS_2) [17] are given in Tables 3, 4, 5, and 6, respectively. The IR spectral data of the compounds studied suggest that the guest molecules retain the symmetry of the corresponding free molecules.

The most notable spectral feature which merits comment is the following: the CH out-of-plane vibrational bands of the guest molecules are found to be shifted to higher frequencies for both ligands (Tables 4, 5, 6) than those of guest molecules in solutions. Similar positive frequency shifts were observed for Hofmann-type clathrates [12] and explained by the presence of a weak hydrogen bond between π -electrons located above and below the plane of the aromatic ring and the ligand molecules of the host lattice [12, 18]. Therefore, we may reasonably suggest that the frequency shifts in our clathrates are due to the

Table 3 The vibrational wavenumbers (cm^{-1}) of chlorobenzene group in the M-daddn-Ni-G (M = Co, Ni, or Cd; G = chlorobenzene) clathrates^a

Assignment ^b	Liquid chlorobenzene ^b	Calculated frequencies ^c	Cd–Ni–dadn ClBz ^d	Co–Ni–ClBz	Ni–Ni–ClBz	Cd–Ni–ClBz
$\nu(\text{CH}), A_1$	3,087 w,sh	3,096 w	n.o.	3,076 vw	3,078 vw	n.o.
$\nu(\text{CH}), B_2$	3,072 s	3,084 m	3,065 vw	3,067 vw	3,067 vw	3,067 vw
$\nu(\text{CH}), A_1$	3,060 w,sh	3,073 w	n.o.	n.o.	n.o.	n.o.
$\nu(\text{CH}), A_1$	3,030 w,sh	3,064 vw	n.o.	n.o.	n.o.	n.o.
$\nu(\text{CH}), B_1$	3,006 w	n.o.	n.o.	n.o.	n.o.	n.o.
$\nu(\text{CC}), B_2$	1,586 s	1,574 w	1,584 s	n.o.	n.o.	n.o.
$\nu(\text{CC}), A_1$	1,571 w,sh	1,570 s	1,561 vw	1,560 vw	1,561 vw	1,559 vw
$\nu(\text{CC}), A_1$	1,479 vs	1,459 vs	1,470 vs	1,475 vs	1,475 vs	1,474 vs
$\nu(\text{CC}), B_2$	1,447 s	1,429 m	1,444 vw	1,445 vw	1,444 vw,sh	1,444 vw
$\beta(\text{CH}), A_1$	1,123 w	1,144 vw	n.o.	n.o.	n.o.	n.o.
$\beta(\text{CH}), B_2$	1,084 s	1,061 vs	1,083 w	1,084 m	1,084 m	1,084 m
$\beta(\text{CH}), B_2$	1,069 vw	1,060 w	1,066 vw	1,066 w	1,065 w	1,066 w
$\beta(\text{CH}), A_1$	1,023 m	1,008 m	1,020 vw	n.o.	n.o.	n.o.
$\gamma(\text{CH}), B_1$	1,003 vw	982 m	n.o.	n.o.	n.o.	n.o.
$\gamma(\text{CH}), B_1$	902 vw	888 w	907 vw	903 vw	905 vw	904 vw
$\gamma(\text{CH}), B_1$	741 vs	729 vs	748 vs	747 vs	745 vs	747 vs
$\delta(\text{ring}), B_1$	702 s	684 s	702 s	703 s	702 s	702 s
$\delta(\text{ring}), B_2$	678 s	680 s	687 m	686 s	687 s	687 s
$\delta(\text{ring}), B_1$	471 m	464 m	469 w	469 w	469 w	469 w

^a ν very, s strong, m medium, w weak, sh shoulder, $n.o.$ not observed, ^b Taken from Ref [15, 16], ^c Calculated vibrational frequencies on the basis set (6-311G(d,p)) of the DFT (B3LYP), ^d Taken from Ref [1]

Table 4 The vibrational wavenumbers (cm^{-1}) of 1,2 dichlorobenzene group for the M-daddn-Ni-G (M = Co, Ni, or Cd; G = 1,2-dichlorobenzene) clathrates^a

Assignment ^b	1,2 ClBz ^b (gas phase)	Calculated frequencies ^c	Cd–Ni–dadn-1,2ClBz ^d	Co–Ni-1,2ClBz	Ni–Ni-1,2ClBz	Cd–Ni-1,2ClBz
$\nu(\text{CH})$, A_1	3,072	3,097 vw	3,058 vw	3,058 vw	3,065 vw	3,060 vw
$\nu(\text{CC})$, A_1	1,576	1,564 w	1,587 vs	1,575 vs	1,574 vs	1,574 vs
$\nu(\text{CC})$, A_1	1,458	1,441 vs	1,456 s	1,456 s	1,456 s	1,456 s
$\nu(\text{CC})$, B_2	1,438	1,414 m	1,435 m	1,436 m	1,437 m	1,436 m
$\beta(\text{CH})$, B_2	1,252	1,266 vw	1,252 w	1,254 w	1,253 w	1,254 w
x-sens., A_1	1,155	1,147 vw	1,155 m	1,157 w	1,158 w	1,158 w
x-sens., B_2	1,130	1,113 w	1,124 m	1,128 s	1,128 s	1,129 s
$\beta(\text{CH})$, B_2	1,038	1,023 m	1,036 s	1,035 s	1,036 s	1,036 s
$\gamma(\text{CH})$, A_2	975	962 vw	969 w,sh	n.o.	n.o.	n.o.
$\gamma(\text{CH})$, B_1	940	826 w	944 vw	959 s	963 s	953 s
$\gamma(\text{CH})$, A_2	850	839 vw	863 vw	847 vw	845 vw	860 vw
$\gamma(\text{CH})$, B_1	748	734 vs	759 vs	756 s	757 s	756 s
x-sens., B_2	740	721 s	737 s	749 m	748 m	748 m
x-sens., A_1	660	686 vw	659 s	660 m	660 m	660 m
x-sens., A_1	480	505 vw	484 vw	472 vw	472vw	474 vw
$\phi(\text{CC})$, B_1	435	461 m	437 s,sh	n.o.	n.o.	n.o.
x-sens., B_2	427	435 w	411 vw	418 vw	417 vw	417 vw,sh

^a ν very, s strong, m medium, w weak, sh shoulder, $n.o.$ not observed, ^b Taken from Ref [17], ^c Calculated vibrational frequencies on the basis set (6-311G(d,p)) of the DFT (B3LYP), ^d Taken from Ref [1]

Table 5 The vibrational wavenumbers (cm^{-1}) of 1,3-dichlorobenzene group for the M-daddn-Ni-G (M = Co, Ni, or Cd; G = 1,3-dichlorobenzene) clathrates^a

Assignment ^b	1,3 ClBz ^b (gas phase)	Calculated frequencies ^c	Cd–Ni–dadn-1,3ClBz ^c	Co–Ni-1,3ClBz	Ni–Ni-1,3ClBz	Cd–Ni-1,3ClBz
$\nu(\text{CH})$, A_1	3,071	3,077 w	3,060 w	3,057 w	3,056 w	3,063 w
$\nu(\text{CC})$, A_1	1,580	1,561 s	1,577 vs	1,576 vs	1,576 vs	1,575 vs
$\nu(\text{CC})$, B_2	1,464	1,443 vs	1,461 vs	1,461 vs	1,461 vs	1,460 vs
$\nu(\text{CC})$, A_1	1,412	1,394 m	1,405 m	1,405 m	1,405 m	1,405 m
$\beta(\text{CH})$, B_2	1,258	1,247 w	1,255 w	1,257 w	1,257 w	1,254 w
x-sens., B_2	1,161	1,150 w	1,162 m	1,160 m	1,162 m	1,159 m
x-sens., B_2	1,127	1,092 m	1,122 m	1,123 m	1,123 m	1,123 m
$\beta(\text{CH})$, B_2	1,079	1,062 s	1,079 m	1,079 m	1,081 m	1,080 m
$\gamma(\text{CH})$, B_1	966	956 vw	996 m,sh	998 m	1,000 m	997 m
$\gamma(\text{CH})$, A_2	896	876 vw	892 w	n.o.	n.o.	n.o.
$\gamma(\text{CH})$, A_2	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.
x-sens., B_2	784	759 vs	781 vs	781 vs	782 vs	782 vs
$\gamma(\text{CH})$, B_1	775	755 vw	n.o.	n.o.	n.o.	n.o.
x-sens., A_1	663	666 m	668 w	673 w	674 w	673 w
x-sens., A_1	428	n.o.	435 s,sh	433 s,sh	434 s,sh	435 s,sh
$\phi(\text{CC})$, B_1	397	384 w	n.o.	n.o.	n.o.	n.o.
x-sens., B_2	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.

^a ν very, s strong, m medium, w weak, sh : shoulder, $n.o.$: not observed, ^b Taken from Ref [17], ^c Calculated vibrational frequencies on the basis set (6-311G(d,p)) of the DFT (B3LYP), ^d Taken from Ref [1]

π -electron donation from the aromatic ring to the hydrogen atoms of the *dadn* and *daddn*, which has a more electrophilic character, caused by the bidentate coordination.

The decrease in the number of G molecules from 1,5 in *dadn* clathrates [1] to 1 in the compounds studied is due to the fact that two of the four cavity units are occupied by the

Table 6 The vibrational wavenumbers (cm⁻¹) of 1,4-dichlorobenzene group for the M-daddn-Ni-G (M = Co, Ni, or Cd; G = 1,4-dichlorobenzene) clathrates^a

Assignment ^b	1,4-dichlorobenzene ^b (gas phase)	Calculated Frequencies ^d	Cd–Ni–dadn-1,4ClBz ^c	Co–Ni-1,4ClBz	Ni–Ni-1,4ClBz	Cd–Ni-1,4ClBz
$\nu(\text{CH}), B_{2u}$	3,087	3,093 vw	n.o.	n.o.	n.o.	n.o.
$\nu(\text{CH}), B_{1u}$	3,078	3,091w	n.o.	n.o.	n.o.	n.o.
$\nu(\text{CC}), B_{1u}$	1,477	1,456 vs	1,475 s,sh	1,475 s	1,476 s	1,475 s,sh
$\nu(\text{CC}), B_{2u}$	1,394	1,375 w	1,392 m	1,390 m	1,391 m	1,391 m
$\alpha(\text{CCC}), B_{1u}$	1,220	1,267 vw	1,223 vw	1,224 vw	1,224 vw	1,223 vw
$\beta(\text{CH}), B_{2u}$	1,107	n.o.	1,097 w,sh	1,101 w,sh	1,104 w,sh	n.o.
$\chi\text{-sens.}, B_{2u}$	1,090	1,064 vw	1,069 w	1,068 w	1,072 w	1,071 w
$\beta(\text{CH}), B_{1u}$	1,015	1,063 vs	1,011 m,sh	1,011 m,sh	1,012 m,sh	1,008 m,sh
$\gamma(\text{CH}), A_u$	951	941 vw	955 m	960 m	959 m	959 m
$\gamma(\text{CH}), B_{3g}$	934	925 vw	943 w,sh	947 w,sh	943 w,sh	947 w,sh
$\gamma(\text{CH}), B_{3u}$	819 ^c	801 vs	815 m,sh	815 m,sh	817 m,sh	815 m,sh
$\chi\text{-sens.}, B_{1u}$	550	521 s	547 w,sh	552 w,sh	549 w,sh	550 w,sh
$\phi(\text{CC}), B_{3u}$	485 ^c	480 m	487 m	486 m	486 m	488 m
$\phi(\text{CC}), A_u$	405	407 vw	n.o.	n.o.	n.o.	n.o.

^a ν very, s strong, m medium, w weak, sh shoulder, $n.o.$ not observed, ^b Taken from Ref [17], ^c Band contour of vapour spectrum, ^d Calculated vibrational frequencies on the basis set (6-311G(d,p)) of the DFT (B3LYP), ^e Taken from Ref [1]

daddn ligands, and the other two cavity units of the host are occupied by the guest molecules. Host–guest interactions are not effective and there is no effect on vibrational bands of the guest molecules raising from 10 to 12 of chain length of the *daddn* ligand molecules.

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