

## Investigation of Host–Guest Interactions in the Hofmann-daddn-type Clathrates: $M(1,12\text{-diaminododecane})Ni(CN)_4 \cdot G$ ( $M = Co, Ni$ or $Cd$ ; $G = \text{toluene, m-xylene, o-xylene}$ or $p\text{-xylene}$ )

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(Received: 17 February 2003; in final form: 5 January 2004)

**Key words:** infrared, spectroscopy, clathrates, 1,12-diaminododecane, toluene, xylene

### Abstract

New Hofmann-diaminododecane-type clathrates of the form  $M(1,12\text{-diaminododecane})Ni(CN)_4 \cdot G$  ( $M = Co, Ni$  or  $Cd$ ;  $G = \text{toluene, m-xylene, o-xylene}$  or  $p\text{-xylene}$ ) have been prepared in powder form and their infrared spectra are reported. The spectral data suggest that the host–guest frameworks of these compounds are similar in structure to other Hofmann-diam-type clathrates.

### Introduction

A series of three-dimensional host lattices,  $Cd(\alpha, \omega\text{-diaminoalkane})Ni(CN)_4$ , has been developed from the two-dimensional Hofmann-type host lattice,  $Cd(NH_3)_2Ni(CN)_4$ , by replacing the ammonia molecules with bidentate ligands with longer carbon chains [1–3]. The strategy was to enlarge the range of guest molecules which can be accommodated in the host lattices. The  $\alpha, \omega$ -diaminoalkane ligands bridge the cadmium atoms in adjacent two-dimensional  $[Cd-Ni(CN)_4]_\infty$  sheets giving three-dimensional host structures, and allow the inclusion of bulky guest molecules [4, 5]. The model of the Hofmann-diam-type host structure is schematically illustrated in Figure 1.

Recently Iwamoto *et al.* [4–7] have reported the crystal structures of  $Cd(NH_2(CH_2)_nNH_2)Ni(CN)_4 \cdot xG$  ( $n = 3–10$ ). The crystal structure studies show that the clathrates in this series are not isomorphous with each other, but that they have Hofmann-type structures and compare with the Hofmann-type and analogous series, which are isostructural [5].

Infrared spectroscopic studies play an important role in investigating host structures due to the host–guest interactions. In our previous papers [8–12], the infrared spectra of the Hofmann-type clathrates show that their host structures are similar to those of Hofmann-en-type clathrates.

In the present work we have extended these studies and prepared  $M(1,12\text{-diaminododecane})Ni(CN)_4 \cdot G$  ( $M = Co, Ni$  or  $Cd$ ;  $G = \text{toluene, m-xylene, o-xylene}$  or  $p\text{-xylene}$ ) (abbreviated to  $M\text{-daddn-Ni-G}$ ) compounds for the first time and report their infrared spectra with the aim of searching for structure–spectra correlations. We give in detail the infrared wavenumbers of the daddn molecule related to its interac-

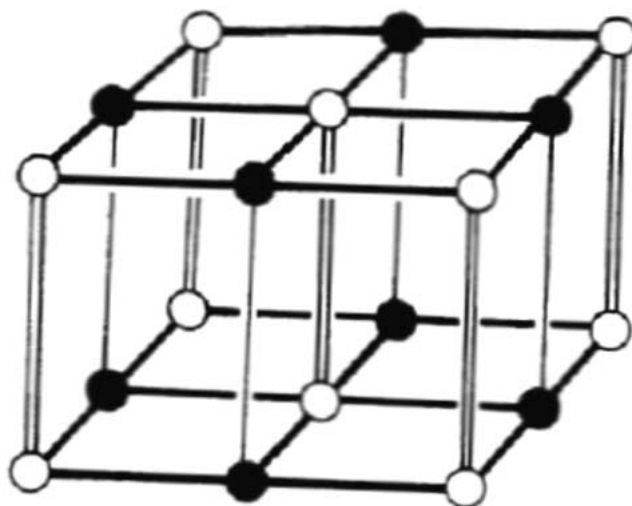


Figure 1. The model of the Hofmann-type host structure. Open circle: 6-coordinate M; solid circle: square-planar Ni; open column: an ambident ligand; thick line: CN bridged; thin line: edge of cavity [14].

tion with different guest molecules and to the presence of different transition metals.

### Experimental

All chemicals used were reagent grade (Merck) and used without further purification. The clathrates  $M(\text{daddn})Ni(CN)_4 \cdot G$  ( $M = Co, Ni$  or  $Cd$ ;  $G = \text{toluene, m-xylene, o-xylene}$  or  $p\text{-xylene}$ ) were prepared by adding one millimole 1,12-diaminododecane and one millimole  $K_2Ni(CN)_4$  solution in 30 mL of water (heated to about 60 °C) to one millimole of  $MCl_2$  solution in 20 mL of water saturated with guest molecules (two millimole toluene, m-xylene, o-xylene or p-xylene). The precipitates were mixed and stirred for two

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Table 1. The analytical results (found%/calculated%) of the compounds

Compounds	C	H	N
Co(NH <sub>2</sub> (CH <sub>2</sub> ) <sub>12</sub> NH <sub>2</sub> ).Ni(CN) <sub>4</sub> .C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )	53.60/53.72	6.86/7.00	16.25/16.34
Ni(NH <sub>2</sub> (CH <sub>2</sub> ) <sub>12</sub> NH <sub>2</sub> ).Ni(CN) <sub>4</sub> .C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )	53.64/53.75	6.84/7.00	16.22/16.30
Cd(NH <sub>2</sub> (CH <sub>2</sub> ) <sub>12</sub> NH <sub>2</sub> ).Ni(CN) <sub>4</sub> .C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )	48.32/48.66	6.22/6.34	14.72/14.80
Co(NH <sub>2</sub> (CH <sub>2</sub> ) <sub>12</sub> NH <sub>2</sub> ).Ni(CN) <sub>4</sub> .m-C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub>	54.48/54.57	7.12/7.19	15.75/15.91
Ni(NH <sub>2</sub> (CH <sub>2</sub> ) <sub>12</sub> NH <sub>2</sub> ).Ni(CN) <sub>4</sub> .m-C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub>	54.48/54.59	7.09/7.20	15.84/15.92
Cd(NH <sub>2</sub> (CH <sub>2</sub> ) <sub>12</sub> NH <sub>2</sub> ).Ni(CN) <sub>4</sub> .m-C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub>	48.35/49.55	6.48/6.53	14.09/14.45
Co(NH <sub>2</sub> (CH <sub>2</sub> ) <sub>12</sub> NH <sub>2</sub> ).Ni(CN) <sub>4</sub> .o-C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub>	54.42/54.57	7.04/7.19	15.64/15.91
Ni(NH <sub>2</sub> (CH <sub>2</sub> ) <sub>12</sub> NH <sub>2</sub> ).Ni(CN) <sub>4</sub> .o-C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub>	54.47/54.59	7.18/7.20	15.86/15.92
Cd(NH <sub>2</sub> (CH <sub>2</sub> ) <sub>12</sub> NH <sub>2</sub> ).Ni(CN) <sub>4</sub> .o-C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub>	49.52/49.55	6.48/6.53	14.39/14.45
Co(NH <sub>2</sub> (CH <sub>2</sub> ) <sub>12</sub> NH <sub>2</sub> ).Ni(CN) <sub>4</sub> .p-C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub>	54.50/54.57	7.15/7.19	15.85/15.91
Ni(NH <sub>2</sub> (CH <sub>2</sub> ) <sub>12</sub> NH <sub>2</sub> ).Ni(CN) <sub>4</sub> .p-C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub>	54.42/54.59	7.12/7.20	15.89/15.92
Cd(NH <sub>2</sub> (CH <sub>2</sub> ) <sub>12</sub> NH <sub>2</sub> ).Ni(CN) <sub>4</sub> .p-C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub>	49.52/49.55	6.50/6.53	14.40/14.45

days, then the precipitates were filtered, washed with ethanol and ether, successively, and kept under guest molecule vapour.

The freshly prepared compounds were analyzed for C, H and N by a LECO CHSN-932 analyzer (found%/calculated%) as seen in Table 1. These analytical results are often poor for the samples obtainable in powder form, due to partial decomposition.

The infrared spectra were recorded between (4000–400 cm<sup>-1</sup>) on a Mattson 1000 FTIR spectrometer, which was calibrated using an indene/comphor/cyclohexane standard solution. The samples were prepared as mulls in nujol and hexachlorobutadiene between KBr plates.

## Results and discussion

The infrared (IR) spectra of the host moieties in the compounds M–Ni–G (M = Co, Ni or Cd; G = toluene, m-xylene, o-xylene or p-xylene) are found to be very similar. These similarities suggest that they also have similar structural features and degrees of the interactions of the guest molecules, *daddn* ligands and Ni(CN)<sub>4</sub> species with their surroundings are almost the same for each compound. It may be most convenient to divide the vibrations into three groups arising from the *daddn* ligands, from the Ni(CN)<sub>4</sub> units and from the guest moieties, respectively. The spectral bands due to the M(CN)<sub>4</sub> and guest species are straightforward and picked out with ease [8–13]. The vibrational wavenumbers of the bands in the spectra of these species are tabulated in Tables 2–7, respectively, together with some relevant spectral data for comparison.

The assignments and the wavenumbers of the infrared bands of the *daddn* molecule observed in the spectra of the compounds under study are given in Table 2, together with the spectral data for *daddn* in solution in CCl<sub>4</sub> [12]. The bands observed in the range of 3347–3273 cm<sup>-1</sup> (Table 2) assigned to the NH<sub>2</sub> stretching frequencies, which are lower than the corresponding values of the free *daddn* molecule, are characteristic of a coordinated –NH<sub>2</sub> group. The absence of the splitting of the symmetric and asymmetric N–H bands

of NH<sub>2</sub> groups suggest the bidentate coordination of the ligand molecules. From the present spectral data, it is not possible to obtain the conformation of the *daddn* molecules in the compounds.

In assigning the bands attributable to the [Ni(CN)<sub>4</sub>]<sup>2-</sup> ion in the spectra of our compounds we refer to the work of McCullough *et al.* who presented vibrational data for the [Ni(CN)<sub>4</sub>]<sup>2-</sup> ion in Na<sub>2</sub>Ni(CN)<sub>4</sub> [17]. The structural studies on these salts have shown that the [Ni(CN)<sub>4</sub>]<sup>2-</sup> ion is not coordinated to the cations [17]. Therefore, it can be treated as an isolated unit and thus used as a reference to observe the effect on the vibrations when coordination to the metals M takes place. The vibrational data for Ni(CN)<sub>4</sub> groups in the compounds studied are given in Table 3 together with the vibrational wavenumbers of Na<sub>2</sub>Ni(CN)<sub>4</sub>.

The assigned wavenumbers of the stretching modes for the Ni(CN)<sub>4</sub> group in the compounds studied appear to be much higher than those of isolated Ni(CN)<sub>4</sub> units (Table 3). Such frequency shifts have been observed for other Hofmann-type clathrates [13], in which both ends of the CN group are coordinated and explained as the mechanical coupling of the internal modes of Ni(CN)<sub>4</sub> with the metal (M) – NC vibrations [8–13]. It follows that the N-ends of Ni(CN)<sub>4</sub> units are also bound to an M atom in our compounds. The fundamental band frequencies of the Ni(CN)<sub>4</sub> group are found to be similar to those of the Hofmann-type clathrates [8–13], suggesting that coordination about the Ni atom is square planar and the [M–Ni(CN)]<sub>∞</sub> layers have been preserved.

The assignments and the wavenumbers of the bands arising from the guest molecules observed in the IR spectra of M–Ni–G (M = Co, Ni or Cd; G = toluene, m-xylene, o-xylene or p-xylene) compounds are given in Tables 4–7, respectively, together with the wavenumbers of the free guest molecule on which the assignments are based. The assignments of molecule wavenumbers in the infrared spectra of the clathrate compounds were based on the studies of Hitchcock and Laposa [18] and Green [19–21], respectively.

The most outstanding spectral features are the following. Several modes of the toluene molecule (–CH<sub>3</sub>) have upward shifts in frequency compared to those in the free

Table 2. The vibrational wavenumbers ( $\text{cm}^{-1}$ ) of 1,12-diaminododecane in the M-Ni-G (M=Co, Ni or Cd, G=toluene, m-xylene, o-xylene or p-xylene).

Assignment <sup>a</sup>	daddn in $\text{CCl}_4^b$	Co-Ni-T	Ni-Ni-T	Cd-Ni-T	Co-Ni-m	Ni-Ni-m	Cd-Ni-m	Co-Ni-o	Ni-Ni-o	Cd-Ni-o	Co-Ni-p	Ni-Ni-p	Cd-Ni-p
$\nu_2(\text{NH}_2)$	3364 m	3340 m	3347 m	3342 m	3336 m	3338 m	3336 m	3341 m	3337 m	3337 m	3343 m	3336 m	3336 m
$\nu_3(\text{NH}_2)$	3330 s	3285 m	3287 m	3285 m	3274 m	3287 m	3281 m	3284 m	3274 m	3273 m	3288 m	3274 m	3273 m
$\nu_4(\text{CH}_2)$	2920 vs	2922 vs	2921 vs	2919 vs	2922 vs	2920 vs	2920 vs	2923 vs	2922 vs	2920 vs	2925 vs	2921 vs	2922 vs
$\nu_5(\text{CH}_2)$	2849 vs	2851 vs	2850 vs	2850 vs	2852 vs	2850 vs	2850 vs	2851 vs	2851 vs	2851 vs	2851 vs	2851 vs	2850 vs
$\delta(\text{NH}_2)$	1605 w,sh	1601 w,sh	1601 w,sh	1602 w,sh	1605 w,sh	1603 w,sh	1601 w,sh	1600 w,sh	1600 w,sh	1601 w,sh	1600 w,sh	1600 w,sh	1601 w,sh
$\delta(\text{NH}_2)$	1578 vs	1584 vs	1586 vs	1587 vs	1583 vs	1587 vs	1589 vs	1586 vs	1584 vs	1587 vs	1587 vs	1589 vs	1589 vs
$\delta(\text{CH}_2)$	1490 m,sh	1494 w	1494 w	1493 w	1490 w	1489 w	1491 w	1496 w	1490 w	1499 w	1498 w	1494 w	1498 w
$\delta(\text{CH}_2)$	1464 s	1468 s	1468 s	1469 s	1470 s	1472 s	1469 s	1469 s	1471 s	1472 s	1468 s	1470 s	1470 s
$\delta(\text{CH}_2)$	1437 w	1438 w	1441 w	1441 w	1438 w	1439 w	1440 w	1441 w	1441 w	1442 w	1441 w	1439 w	1442 w
$\rho_w(\text{CH}_2)$	1393 w	1396 w	1398 w	1395 w	1395 w	1396 w	1398 w	1397 w	1397 w	1398 w	1395 w	1396 w	1398 w
$\rho_w(\text{CH}_2)$	1367 w	1386 w	1385 w	1385 w	1388 w	1384 w	1388 w	1386 w	1386 w	1387 w	1381 w	1380 w	1386 w
$\rho_t(\text{CH}_2)$	1346 w	1359 w	1363 w	1367 w	1360 w	1362 w	1364 w	1368 w	1368 w	1368 w	1366 w	1366 w	1368 w
$\rho_t(\text{CH}_2)$	1321 w	1337 w	1336 w	1334 w	1341 w	1338 w	1339 w	1332 w	1334 w	1337 w	1340 w	1338 w	1339 w
$\rho_t(\text{NH}_2)$	1302 w	1305 w	1308 w	1308 w	1306 w	1308 w	1308 w	1308 w	1308 w	1306 w	1308 w	1038 w	1305 w
$\nu(\text{CN})$	1098 w	1109 m	1111 m	1104 m	1109 m	1102 m	1101 m	1108 m	1110 m	1107 m	1108 m	1101 m	1105 m
$\nu(\text{CN})$	1065 s	1079 w	1080 w	1080 w	1082 w	1084 w	1078 w	1084 w	1080 w	1077 w	1084 w	1080 w	1082 w
$\nu(\text{CN})$	1061 s	1062 m	1061 m	1058 m	1061 m	1062 m	1058 m	1059 m	1057 m	1056 m	1060 m	1057 m	1057 m
$\nu(\text{CC})$	1020 w	1028 s	1030 s	1023 s	1030 s	1026 m	1025 m	1027 s	1026 s	1025 s	1027 s	1026 s	1026 s
$\rho_w(\text{NH}_2)$	1004 m	1004 m	1011 m	n.o.	1004 m	1001 m	1009 m	1008 m	1015 m	1016 m	1009 m	1015 m	1010 m
$\rho_w(\text{NH}_2)$	982 s	978 w	980 w	982 w	979 w	982 w	981 w	981 w	983 w	981 w	981 w	981 w	981 w
$\rho_w(\text{NH}_2)$	934 w	938 w	938 w	939 w	938 w	938 w	935 w	937 w	941 w	941 w	936 w	936 w	935 w
$\rho_w(\text{NH}_2)$	913 s	917 w	921 w	918 w	921 w	922 w	922 w	921 w	920 w	921 w	918 w	919 w	922 w
$\rho_t(\text{CH}_2)$	897 s	894 w	894 w	879 w	891 w	892 w	892 w	891 w	892 w	890 w	890 w	893 w	890 w
$\rho_t(\text{CH}_2)$	819 w	832 w	834 w	n.o.	833 w	835 w	838 w	833 w	n.o.	838 w	832 w	829 w	838 w
$\rho_t(\text{CH}_2)$	731 m	738 m,sh	739 m,sh	739 m,sh	741 m,sh	739 m,sh	740 m,sh	738 m,sh	739 m,sh	738 m,sh	737 m,sh	739 m,sh	738 m,sh
$\rho_t(\text{CH}_2)$	722 s	724 m	724 m	725 m	723 m	720 m	725 m	723 m	720 m	724 m	727 m	720 m	723 m
$\delta(\text{skeletal})$	480 w	495 w	500 w	499 w	492 w	499 w	496 w	499 w	492 w	496 w	499 w	493 w	496 w

<sup>a</sup> Taken From Ref. [16]. <sup>b</sup> Taken From Ref. [12]. v = very, s = strong, m = medium, w = weak, and sh = shoulder, n.o. = not observed.

Table 3. The vibrational wavenumbers ( $\text{cm}^{-1}$ ) of the  $\text{Ni}(\text{CN})_4$  group for the M-Ni-G (M=Co, Ni or Cd; G=toluene, m-xylene, o-xylene or p-xylene) clathrates. (T: toluene, m: m-xylene, o: o-xylene or p: p-xylene).

Assignment <sup>a</sup>	$\text{Na}_2\text{Ni}(\text{CN})_4^{\text{a}}$	Co-Ni-T	Ni-Ni-T	Cd-Ni-T	Co-Ni-m	Ni-Ni-m	Cd-Ni-m
$\nu_8(\text{CN})$ , Eu	2132	2154 vs	2159 vs	2148 vs	2152 vs	2164 vs	2147 vs
Hot Band?	2128	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.
$\nu_9(\text{NiC})$ , Eu	543	555 m	578 m	537 m	553 m	582 m	539 m
$\nu_9(\text{NiC})$ , Eu	–	539 w,sh	555 w,sh	524 vw	539 w,sh	541 w,sh	526 vw
$\pi(\text{NiC})$ , $A_{2u}$	448	452 vw	456 vw	449 vw	450 vw	453 vw	445 vw
$\delta(\text{NiCN})$ , Eu	433	434 vs	437 vs	423 vs	433 vs	438 vs	423 vs
Assignment <sup>a</sup>	$\text{Na}_2\text{Ni}(\text{CN})_4^{\text{a}}$	Co-Ni-o	Ni-Ni-o	Cd-Ni-o	Co-Ni-p	Ni-Ni-p	Cd-Ni-p
$\nu_8(\text{CN})$ , Eu	2132	2155 vs	2160 vs	2146 vs	2155 vs	2160 vs	2147 vs
Hot Band?	2128	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.
$\nu_9(\text{NiC})$ , Eu	543	555 m	580 m	524 m	553 m	580 m	522 m
$\pi(\text{NiC})$ , $A_{2u}$	448	453 vw	455 vw	443 vw	455 vw	455 vw	444 vw
$\delta(\text{NiCN})$ , Eu	433	434 vs	438 vs	423 vs	434 vs	438 vs	423 vs

<sup>a</sup> Taken From Ref. [17]. v = very, s = strong, m=medium, w = weak, and sh = shoulder, n.o.= not observed.

Table 4. The wavenumbers ( $\text{cm}^{-1}$ ) of toluene in M-daddn-Ni-T (M = Co, Ni or Cd; T: toluene).

Assignment <sup>a</sup>	Liquid Toluene	Co-Ni-T	Ni-Ni-T	Cd-Ni-T
$\nu(\text{CH})$ , $A_1$	3085	3081 vw	3084 vw	3084 vw
$\nu(\text{CH})$ , $A_1$	3070	n.o.	n.o.	n.o.
$\nu(\text{CH})$ , $A_1$	3058	n.o.	n.o.	n.o.
$\nu(\text{CH})$ , $B_2$	3037	n.o.	n.o.	n.o.
$\nu(\text{CH})$ , $B_2$	3028	3018 vw	3023 vw	3024 vw
$\nu(\text{CH}_3)$ , $B_1$	2979	2981 w	2979 w	2985 w
$\nu(\text{CH}_3)$ , $B_2$	2950	2953 vw	2952 vw	2951 vw
$\nu(\text{CH}_3)$ , $A_1$	2920	2931 w,sh	2930 w,sh	2930 w,sh
$\nu(\text{CC})$ , $A_1$	1604	n.o.	n.o.	n.o.
$\nu(\text{CC})$ , $B_2$	1584	1590 s,sh	1591 s,sh	1597 s,sh
$\nu(\text{CC})$ , $A_1$	1493	n.o.	n.o.	n.o.
$\delta(\text{CH}_3)$ , $B_2$	1455	1478 m,sh	1478 m,sh	1478 m,sh
$\delta(\text{CH}_3)$ , $A_1$	1378	n.o.	n.o.	n.o.
$\nu(\text{CC})$ , $B_2$	1331	1341 vw	1335 vw	1343 vw
$\beta(\text{CH})$ , $B_2$	1313	1310 vw	1309 vw	1310 vw
$\nu(\text{C}-\text{CH}_3)\text{X-sens}$ , $A_1$	1208	n.o.	n.o.	n.o.
$\beta(\text{CH})$ , $A_1$	1176	1179 vw	1179 vw	1179 vw
$\beta(\text{CH})$ , $B_2$	1153	1159 vw	1157 vw	1155 vw
$\beta(\text{CH})$ , $B_2$	1080	n.o.	n.o.	n.o.
$\tau(\text{CH}_3)$ , $B_1$	1040	1043 vw	1043 vw	1040 vw
$\beta(\text{CH})$ , $A_1$	1028	1025 w,sh	1025 w,sh	1020 w,sh
Ring, $A_1$	1002	1001 w,sh	1008 w,sh	n.o.
$\gamma(\text{CH})$ , $B_1$	983	n.o.	n.o.	n.o.
$\gamma(\text{CH})$ , $B_1$	893	n.o.	n.o.	n.o.
$\alpha(\text{CCC})\text{X-sens}$ , $A_1$	784	788 vw	785 vw	790 vw
$\gamma(\text{CH})$ , $B_1$	734	737 s	737 s	737 s
$\phi(\text{CC})$ , $B_2$	690	696 m	696 m	696 m
?	–	n.o.	n.o.	n.o.
$\alpha(\text{CCC})$ , $B_2$	620	616 vw	n.o.	n.o.
$\alpha(\text{CCC})\text{X-sens}$ , $A_1$	524	539 vw	539 vw	527 vw
$\phi(\text{CCC})\text{X-sens}$ , $B_1$	467	464 m	465 m	464 m

<sup>a</sup> Taken from Ref [18]. v = very, s = strong, m = medium, w = weak, br = broad, sh = shoulder, n.o. = not observed.

Table 5. The wavenumbers ( $\text{cm}^{-1}$ ) of m-xylene in M-daddn-Ni-m (M = Co, Ni or Cd; m: m-xylene).

Assignment <sup>a</sup>	m-xylene <sup>a</sup>	Co-Ni-m	Ni-Ni-m	Cd-Ni-m
$\nu(\text{CH}), B_2$	3052	n.o.	n.o.	n.o.
$\nu(\text{CH}), A_1$	3032	n.o.	n.o.	n.o.
$\nu(\text{CC}), B_2$	1613	1616 w	1616 w	1615 w
$\nu(\text{CC}), A_1$	1595	1599 vw	1601 vw	1598 vw
$\nu(\text{CC}), B_2$	1492	1497 vw	1499 vw	1500 vw
$\nu(\text{CC}), A_1$	1460	1468 w	1469 w	1467 w,sh
$\beta(\text{CH}), B_2$	1303	n.o.	n.o.	n.o.
$\alpha(\text{CCC}), B_2$	1264	1280 vw	1279 vw	1278 vw
X-sens., $A_1$	1252	1258 vw	1250 vw	1252 vw
$\beta(\text{CH}), B_2$	1167	1166 vw	1163 vw	1165 vw
X-sens., $B_2$	1154	1153 vw	1152 vw	1152 vw
$\beta(\text{CH}), A_1$	1094	1086 vw	1093 vw	1092 vw
$\gamma(\text{CH}), B_1$	968	959 vw	967 vw	959 vw
X-sens., $B_2$	905	n.o.	n.o.	n.o.
$\gamma(\text{CH}), B_1$	876	n.o.	n.o.	n.o.
$\gamma(\text{CH}), B_1$	768	768 vw	769 vw	768 vw
X-sens., $A_1$	724	n.o.	n.o.	n.o.
$\pi(\text{CC}), B_1$	690	693 w	691 w	696 w
X-sens., $A_1$	537	n.o.	n.o.	n.o.
X-sens., $B_2$	515	520 vw	521 vw	521 vw
$\pi(\text{CC}), B_1$	433	431 vw	434 vw	434 vw
X-sens., $B_2$	404	402 vw	403 vw	401 vw

<sup>a</sup>Taken from Ref [19].  $\nu$  = very, s = strong, m = medium, w = weak, br = broad, sh = shoulder, n.o = not observed.

Table 6. The wavenumbers ( $\text{cm}^{-1}$ ) of o-xylene in M-daddn-Ni-o (M = Co, Ni or Cd; o: o-xylene).

Assignment <sup>a</sup>	o-xylene	Co-Ni-o	Ni-Ni-o	Cd-Ni-o
$\nu(\text{CH}), B_2$	3080	3107 w	3108 w	3109 w
$\nu(\text{CH}), A_1$	3064	n.o.	n.o.	n.o.
$\nu(\text{CH}), B_2$	3048	3053 vw	3056 vw	3054 vw
$\nu(\text{CC}), A_1$	1494	1506 w	1508 w	1506 w
$\nu(\text{CC}), B_2$	1468	1492 m	1492 m	1496 m
Kekulé, $A_1$	1292	n.o.	n.o.	n.o.
$\beta(\text{CH}), B_2$	1290	1295 vw	1291 vw	1295 vw
X-sens., $A_1$	1222	1219 vw	1221 vw	1220 vw
X-sens., $B_2$	1185	1180 w	1180 w	1181 w
$\beta(\text{CH}), A_1$	1155	1166 w	1164 w	1165 w
$\beta(\text{CH}), B_2$	1121	1115 w	1116 w	1115 vw
$\beta(\text{CH}), A_1$	1052	1052 w	1054 w	1053 w
$\gamma(\text{CH}), B_1$	930	925 w	928 w	928 vw
$\gamma(\text{CH}), A_2$	860	872 vw	862 vw	863 vw
X-sens., $B_2$	826	n.o.	n.o.	n.o.
$\gamma(\text{CH}), B_1$	741	750 vs	746 vs	745 vs
X-sens., $A_1$	581	599 m	597 m	599 m
X-sens., $B_2$	505	500 vw	500 vw	500 vw
$\phi(\text{CC}), B_1$	435	454 vw	454 vw	455 vw
X-sens., $B_2$	406	408 vw	407 vw	410 vw

<sup>a</sup> Taken from Ref [20].  $\nu$  = very, s = strong, m = medium, w = weak, n.o. = not observed.

Table 7. The wavenumbers ( $\text{cm}^{-1}$ ) of p-xylene in M-daddn-Ni-p (M = Co, Ni or Cd; p: p-xylene).

Assignment <sup>a</sup>	Liquid p-xylene	Co-Ni-p	Ni-Ni-p	Cd-Ni-p
$\nu(\text{CH}), B_{1u}$	3044	3045 vw	3047 vw	3046 vw
$\nu(\text{CH}), B_{2u}$	3017	3019 vw	3023 vw	3021 vw
$\nu(\text{CH}_3), B_{2u}$	2975	2947	2980 vw	2948 vw
	2983 vw	2947 vw	2982 vw	2947 vw
$\nu(\text{CH}_3), B_{3u}$	2923	2928 w,sh	2930 w,sh	2929 w,sh
$\nu(\text{CC}), B_{1u}$	1529	1516 w	1513 w	1511 w
$\delta(\text{CH}_3), B_{3u}$	1458	1452	1473 w,sh	n.o.
	1474 w,sh	n.o.	1473 w,sh	n.o.
$\nu(\text{CC}), B_{2u}$	1421	1432 vw	1432 vw	1432 vw
$\delta(\text{CH}_3), B_{1u}$	1379	n.o.	n.o.	n.o.
$\alpha(\text{CCC}), B_{2u}$	1324	n.o.	n.o.	n.o.
X-sens., $B_{1u}$	1220	1221 vw	1222 vw	1233 vw
$\beta(\text{CH}), B_{2u}$	1120	1118 w,sh	n.o.	1119 w,sh
$\tau(\text{CH}_3), B_{2u}$	1041	1041 m	1042 m	1041 m
$\beta(\text{CH}), B_{1u}$	1023	1022 w,sh	1022 w,sh	1021 w,sh
$\gamma(\text{CH}), B_{3u}$	795	797 vs	797 vs	798 vs
X-sens., $B_{1u}$	725	732 m	727 m	727 m
$\phi(\text{CC}), B_{3u}$	438	484 m	484 m	487 m

<sup>a</sup>Taken from Ref [21]. v = very, s = strong, m = medium, w = weak, br = broad, sh = shoulder, n.o. = not observed.

guest molecules. These shifts may occur due to the effect of weak hydrogen bonding. Another feature of CH out-of-plane vibrational bands of m-xylene, o-xylene and p-xylene is found to be shifted to a higher wavenumber from that of liquid guest molecules as seen in Table 5–7. Similar positive shifts have been observed for Hofmann-type clathrates [13, 14]. This shift was explained for this type of clathrates [13] by the presence of a weak hydrogen bonding.

The preceding discussion considered together leads us to the conclusion that the compounds M(daddn)Ni(CN)<sub>4</sub>.G (M = Co, Ni or Cd; G = toluene, m-xylene, o-xylene or p-xylene) are similar in structure to the other Hofmann-diam-type clathrates.

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