

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

T. R. SERTBAKAN, S. SAĞLAM, A. ÖZBAY and S. ÖZÇELIK*

Deparment of Physics, Faculty of Art and Sciences, University of Gazi, Ankara, 0650, Turkey

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Abstract

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

Introduction

A series of three-dimensional host lattices, $Cd(\alpha, \omega$ diaminoalkane)Ni(CN)₄, has been developed from the twodimensional 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 α , ω -diaminoalkane ligands bridge the cadmium atoms in adjacent two-dimensional [Cd-Ni(CN)₄]_{∞} 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.

Recenty Iwamoto *et al.* [4–7] have reported the crystal structures of $Cd(NH_2(CH_2)nNH_2)Ni(CN)_4 \text{ xG}$ (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-diaminododecane)Ni(CN)₄.G (M = Co, Ni or Cd; G = toluene, m-xylene, o-xylene or p-xylene) (abbreviated to M-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(daddn) Ni(CN)₄.G (M = Co, Ni or Cd; G = toluene, m-xylene, oxylene or p-xylene) were prepared by adding one millimole 1,12-diaminododecane and one millimole K₂Ni(CN)₄ solution in 30 mL of water (heated to about 60 °C) to one millimole of MCl₂ 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

^{*} Author for correspondence: E-mail: sozcelik@gazi.edu.tr

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

Compounds	С	Н	Ν
Co(NH ₂ (CH ₂) ₁₂ NH ₂).Ni(CN) ₄ .C ₆ H ₅ (CH ₃)	53.60/53.72	6.86/7.00	16.25/16.34
$Ni(NH_2(CH_2)_{12}NH_2).Ni(CN)_4.C_6H_5(CH_3)$	53.64/53.75	6.84/7.00	16.22/16.30
$Cd(NH_2(CH_2)_{12}NH_2).Ni(CN)_4.C_6H_5(CH_3)$	48.32/48.66	6.22/6.34	14.72/14.80
$Co(NH_2(CH_2)_{12}NH_2).Ni(CN)_4.m-C_6H_4(CH_3)_2$	54.48/54.57	7.12/7.19	15.75/15.91
$Ni(NH_2(CH_2)_{12}NH_2).Ni(CN)_4.m-C_6H_4(CH_3)^2$	54.48/54.59	7.09/7.20	15.84/15.92
$Cd(NH_2(CH_2)_{12}NH_2).Ni(CN)_4.m-C_6H_4(CH_3)_2$	48.35/49.55	6.48/6.53	14.09/14.45
$Co(NH_2(CH_2)_{12}NH_2).Ni(CN)_4.o-C_6H_4(CH_3)_2$	54.42/54.57	7.04/7.19	15.64/15.91
$Ni(NH_2(CH_2)_{12}NH_2).Ni(CN)_4.o-C_6H_4(CH_3)^2$	54,47/54.59	7.18/7.20	15.86/15.92
$Cd(NH_2(CH_2)_{12}NH_2).Ni(CN)_{4.0}-C_6H_4(CH_3)_2$	49.52/49.55	6.48/6.53	14.39/14.45
$Co(NH_2(CH_2)_{12}NH_2).Ni(CN)_4.p-C_6H_4(CH_3)_2$	54.50/54.57	7.15/7.19	15.85/15.91
$Ni(NH_2(CH_2)_{12}NH_2).Ni(CN)_4.p-C_6H_4(CH_3)_2$	54.42/54.59	7.12/7.20	15.89/15.92
$Cd(NH_2(CH_2)_{12}NH_2).Ni(CN)_4.p-C_6H_4(CH_3)_2$	49.52/49.55	6.50/6.53	14.40/14.45

days, then the precipitates were filtered, washed with ethenol 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 $(4000-400 \text{ cm}^{-1})$ 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 = tolune, 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)₄ 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)₄ units and from the guest moieties, respectively. The spectral bands due to the M(CN)₄ 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 CCl₄ [12]. The bands observed in the range of 3347-3273 cm⁻¹ (Table 2) assigned to the NH₂ stretching frequencies, which are lower than the corresponding values of the free *daddn* molecule, are characteristic of a coordinated –NH₂ group. The absence of the splitting of the symmetric and asymmetric N–H bands

of NH₂ 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 $[Ni(CN)_4]^{2-}$ ion in the spectra of our compounds we refer to the work of McCullough *et al.* who presented vibrational data for the $[Ni(CN)_4]^{2-}$ ion in Na₂Ni(CN)₄ [17]. The structural studies on these salts have shown that the $[Ni(CN)_4]^{2-}$ 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)₄ groups in the compounds studied are given in Table 3 together with the vibrational wavenumbers of Na₂Ni(CN)₄.

The assigned wavenumbers of the stretching modes for the Ni(CN)₄ group in the compounds studied appear to be much higher than those of isolated Ni(CN)₄ 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)₄ with the metal (M) – NC vibrations [8–13]. It follows that the N-ends of Ni(CN)₄ units are also bound to an M atom in our compounds. The fundamental band frequencies of the Ni(CN)₄ 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)]_{∞} 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 (-CH₃) have upward shifts in frequency compared to those in the free Table 2. The vibrational wavenumbers (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).

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$\delta(NH_2)$ 1578 vs 1584 vs 1586 vs 1587 vs 1583 vs $\delta(CH_2)$ 1490 m,sh 1494 vw 1494 vw 1493 vw 1490 vs $\delta(CH_2)$ 1464 s 1468 s 1468 s 1470 s 1470 s $\delta(CH_2)$ 1437 w 1441 w 1441 w 1470 s 1470 s $\delta(CH_2)$ 1333 w 1338 w 1338 v 1338 v 1338 v $\rho_w(CH_2)$ 1337 w 1335 vw 1336 vw 1336 v $\rho_w(CH_2)$ 1331 w 1335 vw 1336 vw 1360 v $\rho_w(CH_2)$ 1332 vw 1335 vw 1336 vw 1360 v $\rho_v(CH_2)$ 1320 vw 1335 vw 1336 vw 1360 v $\rho_v(CH_2)$ 1332 vw 1336 vw 1360 v 100 m $\rho_v(NH_2)$ 1302 w 1336 vw 1360 v 1000 m 1000 m	1587 vs 1583 vs 1493 vw 1490 vw 1469 s 1470 s 1441 w 1438 vw 1395 vw 1395 vw 1385 vw 1388 vw 1367 vw 1360 vw 1368 vw 1360 vw	1587 vs 158 1489 vw 149 1472 s 144 1472 s 144 1439 vw 144 1396 vw 133 1382 vw 133 1338 vw 133	 39 vs 1586 v; 11 vw 1406 v 1469 s 59 s 1469 s 1441 v 1441 v 1441 v 1347 v 1386 v 1386 v 1332 v 1332 v 	s 1584 vs w 1490 vw 1471 s w 1441 vw w 1397 vw w 1386 vw w 1368 vw	1587 vs 1499 vw 1472 s 1442 w 1398 vw 1387 vw	1587 vs 1498 vw 1468 s 1441 vw 1395 vw 1381 vw	1589 vs 1494 vw 1470 s 1439 vw 1396 vw 1366 vw	1589 vs 1498 vw 1470 s 1442 w 1398 vw 1368 vw
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$\rho_w(CH_2)$ 1393 w 1396 vw 1398 vw 1395 vw 1396 vw 1395 vw 1396 vw 1396 vw 1395 vw 1396 vw 1396 vw 1385 vw 1385 vw 1386 vw 1360 v 1020 v 1020 v 1020 v 1000 v 1	1395 vw 1395 vw 1385 vw 1388 vw 1367 vw 1360 vw 1334 vw 1341 vw 1308 vw 1306 vw	1396 vw 139 1384 vw 138 1362 vw 138 1338 vw 133	38 vw 1397 v 38 vw 1386 v 54 vw 1368 v 39 vw 1332 v	w 1397 vw w 1386 vw w 1368 vw	1398 vw 1387 vw	1395 vw 1381 vw	1396 vw 1380 vw 1366 vw	1398 vw 1386 vw 1368 vw
$\rho_w(CH_2)$ 1367 w 1385 ww 1385 ww 1385 ww 1385 ww 1388 w 1386 ww 1360 w 1360 w 1360 w 1360 w 1361 w 1361 w 1361 w 1361 w 1366 w 1060 m 1061 m	1385 vw 1388 vw 1367 vw 1360 vw 1334 vw 1341 vw 1308 vw 1306 vw	1384 vw 138 1362 vw 136 1338 vw 133	38 vw 1386 v 54 vw 1368 v 39 vw 1332 v	w 1386 vw w 1368 vw	1387 vw	1381 vw	1360 vw 1366 vw	1386 vw 1368 vw
$\rho_t(CH_2)$ 1346 w 1359 vw 1363 vw 1367 vw 1360 v $\rho_t(CH_2)$ 1321 vw 1335 vw 1363 vw 1367 vw 1361 v $\rho_t(NH_2)$ 1321 vw 1335 vw 1336 vw 1341 v 1341 v $\rho_t(NH_2)$ 1302 w 1308 vw 1308 vw 1308 vw 1306 v $\nu(CN)$ 1098 w 1109 m 1111 m 1104 m 1109 n $\nu(CN)$ 1065 s 1079 w 1080 w 1082 w 1082 v $\nu(CN)$ 1061 s 1061 m 1010 m 1082 m 1002 m $\nu(CN)$ 1065 s 1079 w 1080 w 1082 m 1004 n $\nu(NH_2)$ 1004 m 1011 m n.o. 1004 n 1004 n $\rho_w(NH_2)$ 982 vw 938 vw 921 v	1367 vw 1360 vw 1334 vw 1341 vw 1308 vw 1306 vw	1362 vw 136 1338 vw 133	54 vw 1368 v 39 vw 1332 v	w 1368 vw			1366 vw	1368 vw
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	1334 vw 1341 vw 1308 vw 1306 vw	1338 vw 133	39 vw 1332 v		1368 vw	1366 vw	** · · · · · · · · · · · · · · · · · ·	
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	1308 vw 1306 vw			w 1334 vw	1337 vw	1340 vw	1338 vw	WV 4661
$ \begin{array}{llllllllllllllllllllllllllllllllllll$		1308 vw 130	38 vw 1308 v	w 1308 w	1306 vw	1308 vw	1038 vw	1305 w
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	1104 m 1109 m	1102 m 110	01 m 1108 m	n 1110 m	1107 m	1108 m	1101 m	1105 m
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	1080 w 1082 w	1084 w 107	78 w 1084 w	/ 1080 w	1077 w	1084 w	1080 w	1082 w
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	1058 m 1061 m	1062 m 105	58 m 1059 m	n 1057 m	1056 m	1060 m	1057 m	1057 m
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1023 s 1030 s	1026 m 102	25 m 1027 s	1026 s	1025 s	1027 s	1026 s	1026 s
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	n.o. 1004 m	1001 m 100	9 m 1008 m	n 1015 m	1016 m	1009 m	1015 m	1010 m
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	982 vw 979 vw	982 vw 98	31 vw 981 v	w 983 vw	981 vw	981 vw	981 vw	981 vw
ρ _w (NH ₂) 913 s 917 vw 921 vw 918 vw 921 v	939 vw 938 vw	938 vw 93	35 vw 937 v	w 941 vw	941 vw	936 vw	936 vw	935 vw
	918 vw 921 vw	922 vw 92	22 vw 921 v	w 920 vw	921 vw	918 vw	919 vw	922 vw
$\rho_{\rm r}({\rm CH_2})$ 897 s 894 vw 894 vw 879 vw 891 v	879 vw 891 vw	892 vw 89	32 vw 891 v	w 892 vw	890 vw	wv 068	893 vw	890 vw
$\rho_{\rm r}({\rm CH}_2)$ 819 w 832 vw 834 vw n.o. 833 v	n.o. 833 vw	835 vw 83	38 vw 833 v	w n.o.	838 vw	832 vw	829 vw	838 vw
$\rho_{\rm r}({\rm CH}_2)$ 731 m 738 m,sh 739 m,sh 739 m,sh 741 n	739 m,sh 741 m,sh	739 m,sh 74	40 m,sh 738 m	1,sh 739 m,sh	738 m,sh	737 m,sh	739 m,sh	738 m,sh
$\rho_{\rm r}({\rm CH_2})$ 722 s 724 m 724 m 725 m 723 n	725 m 723 m	720 m 72	25 m 723 m	л 720 m	724 m	727 m	720 m	723 m
δ (skeletal) 480 w 495 w 500 w 499 w 492 v	499 w 492 w	499 w 49	96 w 499 w	и 492 w	496 w	499 w	493 w	496 w

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

Assignment ^a	Na2Ni(CN)4a	Co-Ni-T	Ni-Ni-T	Cd-Ni-T	Co-Ni-m	Ni–Ni–m	Cd-Ni-m
v8(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.
v9(NiC), Eu	543	555 m	578 m	537 m	553 m	582 m	539 m
v9(NiC), Eu	-	539 w,sh	555 w,sh	524 vw	539 w,sh	541 w,sh	526 vw
π (NiC), A _{2u}	448	452 vw	456 vw	449 vw	450 vw	453 vw	445 vw
δ (NiCN), Eu	433	434 vs	437 vs	423 vs	433 vs	438 vs	423 vs
Assignment ^a	Na2Ni(CN)4 ^a	Co-Ni-o	Ni–Ni–o	Cd–Ni–o	Co–Ni–p	Ni–Ni–p	Cd–Ni–p
Assignment ^a $\nu_8(CN)$, Eu	Na ₂ Ni(CN) ₄ ^a 2132	Co–Ni–o 2155 vs	Ni–Ni–o 2160 vs	Cd–Ni–o 2146 vs	Co–Ni–p 2155 vs	Ni–Ni–p 2160 vs	Cd–Ni–p 2147 vs
Assignment ^a v_8 (CN), Eu Hot Band?	Na ₂ Ni(CN) ₄ ^a 2132 2128	Co–Ni–o 2155 vs n.o.	Ni–Ni–o 2160 vs n.o.	Cd–Ni–o 2146 vs n.o.	Co–Ni–p 2155 vs n.o.	Ni–Ni–p 2160 vs n.o.	Cd–Ni–p 2147 vs n.o.
Assignment ^a $\nu_8(CN)$, Eu Hot Band? $\nu_9(NiC)$, Eu	Na ₂ Ni(CN) ₄ ^a 2132 2128 543	Co–Ni–o 2155 vs n.o. 555 m	Ni–Ni–o 2160 vs n.o. 580 m	Cd–Ni–o 2146 vs n.o. 524 m	Co–Ni–p 2155 vs n.o. 553 m	Ni–Ni–p 2160 vs n.o. 580 m	Cd–Ni–p 2147 vs n.o. 522 m
Assignment ^a $\nu_8(CN)$, Eu Hot Band? $\nu_9(NiC)$, Eu π (NiC), A _{2u}	Na ₂ Ni(CN) ₄ ^a 2132 2128 543 448	Co-Ni-o 2155 vs n.o. 555 m 453 vw	Ni–Ni–o 2160 vs n.o. 580 m 455 vw	Cd-Ni-o 2146 vs n.o. 524 m 443 vw	Co-Ni-p 2155 vs n.o. 553 m 455 vw	Ni–Ni–p 2160 vs n.o. 580 m 455 vw	Cd–Ni–p 2147 vs n.o. 522 m 444 vw

Table 3. The vibrational wavenumbers (cm^{-1}) of the Ni(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).

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

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

Assignment ^a	Liquid Toluene	Co-Ni-T	Ni-Ni-T	Cd-Ni-T
ν(CH), A ₁	3085	3081 vw	3084 vw	3084 vw
ν(CH), A ₁	3070	n.o.	n.o.	n.o.
ν(CH), A ₁	3058	n.o.	n.o.	n.o.
ν(CH), B ₂	3037	n.o.	n.o.	n.o.
ν(CH), B ₂	3028	3018 vw	3023 vw	3024 vw
v(CH ₃), B ₁	2979	2981 w	2979 w	2985 w
v(CH ₃), B ₂	2950	2953 vw	2952 vw	2951 vw
v(CH ₃), A ₁	2920	2931 w,sh	2930 w,sh	2930 w,sh
$\nu(CC), A_1$	1604	n.o.	n.o.	n.o.
$\nu(CC), B_2$	1584	1590 s,sh	1591 s,sh	1597 s,sh
ν (CC), A ₁	1493	n.o.	n.o.	n.o.
$\delta(CH_3), B_2$	1455	1478 m,sh	1478 m,sh	1478 m,sh
$\delta(CH_3), A_1$	1378	n.o.	n.o.	n.o.
$\nu(CC), B_2$	1331	1341 vw	1335 vw	1343 vw
β (CH), B ₂	1313	1310 vw	1309 vw	1310 vw
ν (C–CH ₃)X-sens, A ₁	1208	n.o.	n.o.	n.o.
β (CH), A ₁	1176	1179 vw	1179 vw	1179 vw
β (CH), B ₂	1153	1159 vw	1157 vw	1155 vw
β (CH), B ₂	1080	n.o.	n.o.	n.o.
$\tau(CH_3), B_1$	1040	1043 vw	1043 vw	1040 vw
β (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.
γ (CH), B ₁	983	n.o.	n.o.	n.o.
γ (CH), B ₁	893	n.o.	n.o.	n.o.
α (CCC)X-sens, A ₁	784	788 vw	785 vw	790 vw
γ (CH), B ₁	734	737 s	737 s	737 s
$\phi(CC), B_2$	690	696 m	696 m	696 m
?	-	n.o.	n.o.	n.o.
α (CCC), B ₂	620	616 vw	n.o.	n.o.
α (CCC)X-sens, A ₁	524	539 vw	539 vw	527 vw
$\phi(\text{CCC})$ X-sens, B ₁	467	464 m	465 m	464 m

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

Assignment ^a	m-xylene ^a	Co–Ni–m	Ni–Ni–m	Cd–Ni–m
ν(CH), B ₂	3052	n.o.	n.o.	n.o.
ν (CH), A ₁	3032	n.o.	n.o.	n.o.
$\nu(CC), B_2$	1613	1616 w	1616 w	1615 w
ν (CC), A ₁	1595	1599 vw	1601 vw	1598 vw
$\nu(CC), B_2$	1492	1497 vw	1499 vw	1500 vw
ν (CC), A ₁	1460	1468 w	1469 w	1467 w,sh
β (CH), B ₂	1303	n.o.	n.o.	n.o.
α (CCC), B ₂	1264	1280 vw	1279 vw	1278 vw
X-sens., A1	1252	1258 vw	1250 vw	1252 vw
β (CH), B ₂	1167	1166 vw	1163 vw	1165 vw
X-sens., B ₂	1154	1153 vw	1152 vw	1152 vw
β (CH), A ₁	1094	1086 vw	1093 vw	1092 vw
γ (CH), B ₁	968	959 vw	967 vw	959 vw
X-sens., B ₂	905	n.o.	n.o.	n.o.
γ (CH), B ₁	876	n.o.	n.o.	n.o.
γ (CH), B ₁	768	768 vw	769 vw	768 vw
X-sens., A ₁	724	n.o.	n.o.	n.o.
$\pi(CC), B_1$	690	693 w	691 w	696 w
X-sens., A1	537	n.o.	n.o.	n.o.
X-sens., B ₂	515	520 vw	521 vw	521 vw
$\pi(CC), B_1$	433	431 vw	434 vw	434 vw
X-sens., B ₂	404	402 vw	403 vw	401 vw

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

^aTaken from Ref [19]. v = very, s = strong, m = medium, w = weak, br = broad, sh = shoulder, n.o = not observed.

Assignment ^a	o-xylene	Co-Ni-o	Ni–Ni–o	Cd–Ni–o
ν(CH), B ₂	3080	3107 w	3108 w	3109 w
ν (CH), A ₁	3064	n.o.	n.o.	n.o.
v(CH), B ₂	3048	3053 vw	3056 vw	3054 vw
ν(CC), A ₁	1494	1506 w	1508 w	1506 w
$\nu(CC), B_2$	1468	1492 m	1492 m	1496 m
Kekulé, A ₁	1292	n.o.	n.o.	n.o.
β (CH), B ₂	1290	1295 vw	1291 vw	1295 vw
X-sens., A1	1222	1219 vw	1221 vw	1220 vw
X-sens., B ₂	1185	1180 w	1180 w	1181 w
β (CH), A ₁	1155	1166 w	1164 w	1165 w
β (CH), B ₂	1121	1115 w	1116 w	1115 vw
β (CH), A ₁	1052	1052 w	1054 w	1053 w
γ (CH), B ₁	930	925 w	928 w	928 vw
γ (CH), A ₂	860	872 vw	862 vw	863 vw
X-sens., B ₂	826	n.o.	n.o.	n.o.
γ (CH), B ₁	741	750 vs	746 vs	745 vs
X-sens., A1	581	599 m	597 m	599 m
X-sens., B ₂	505	500 vw	500 vw	500 vw
$\phi(CC), B_1$	435	454 vw	454 vw	455 vw
X-sens., B ₂	406	408 vw	407 vw	410 vw

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

^a Taken from Ref [20]. v = very, s = strong, m = medium, w = weak, n.o. = not observed.

Assignment ^a	Liquid p-xylene	Co-Ni-p	Ni–Ni–p	Cd–Ni–p
ν(CH), B _{1u}	3044	3045 vw	3047 vw	3046 vw
ν(CH), B _{2u}	3017	3019 vw	3023 vw	3021 vw
v(CH3), B2u	2975	2947	2980 vw	2948 vw
	2983 vw	2947 vw	2982 vw	2947 vw
ν (CH ₃), B _{3u}	2923	2928 w,sh	2930 w,sh	2929 w,sh
ν (CC), B _{1u}	1529	1516 w	1513 w	1511 w
$\delta(CH_3), B_{3u}$	1458	1452	1473 w,sh	n.o.
	1474 w,sh	n.o.	1473 w,sh	n.o.
ν (CC), B _{2u}	1421	1432 vw	1432 vw	1432 vw
$\delta(CH_3), B_{1u}$	1379	n.o.	n.o.	n.o.
α (CCC), B _{2u}	1324	n.o.	n.o.	n.o.
X-sens., B _{1u}	1220	1221 vw	1222 vw	1233 vw
β (CH), B _{2u}	1120	1118 w,sh	n.o.	1119 w,sh
τ (CH ₃), B _{2u}	1041	1041 m	1042 m	1041 m
β (CH), B _{1u}	1023	1022 w,sh	1022 w,sh	1021 w,sh
γ (CH), B _{3u}	795	797 vs	797 vs	798 vs
X-sens., B _{1u}	725	732 m	727 m	727 m
$\phi(CC), B_{3u}$	438	484 m	484 m	487 m

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

^aTaken 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-ofplane 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 $M(daddn)Ni(CN)_4$.G (M = Co, Ni or Cd; G = toluene, m-xylene, o-xylene or pxylene) are similar in structure to the other Hofmann-diamtype clathrates.

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