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An Infrared Spectroscopic Study on the Hofmann-diam-type 1,12-Diaminododecanemetal(II) Tetracyanonickelate(II)-aromatic Guest Clathrates: $M(H_2N(CH_2)_{12}NH_2)Ni(CN)_4 \cdot G$(M=Co, Ni or Cd; G = Benzene, Naphthalene, Anthracene, Phenanthrene or Biphenyl)

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Abstract

Three Hofmann-diaminododecane-type clathrates of the form M(1,12-diaminododecane) $Ni(CN)_4 \cdot G$ (M = Co, Ni or Cd; G = benzene, naphthalene, anthracene, phenanthrene or biphenyl) have been prepared in powder form. The 1,12-diaminododecane molecules in the host lattice permit the inclusion of bulky guest molecules. The spectral features suggest that these compounds are similar in structure to the other Hofmann-diam-type clathrates.

Introduction

Hofmann-α,ω-diaminoalkane-type hosts have been developed from the Hofmann-type host lattice, $Cd(NH_3)_2Ni(CN)_4$, by replacing the pair of ammine ligands by the α,ω-diaminoalkane ligands behaving ambidently [1]. Bidentate α,ω-diaminoalkane ligands with long carbon chains give three-dimensional host structures by bridging between the metal atoms (Cd) in the adjacent two-dimensional $\{Cd—Ni(CN)_4\}_\infty$ layers [2].

The model of the Hofmann-diam-type host structure is schematically illustrated in Figure 1.

In our previous papers [3–6], the infrared spectra of the Hofmann-type clathrates showed that their host structures are similar to those of Hofmann-en-type clathrates [1].

In the present work, we have extended these studies and prepared M(daddn)$Ni(CN)_4$.G (M = Co, Ni or Cd; daddn = 1,12-diaminododecane; G = benzene, naphthalene, anthracene, phenanthrene or biphenyl) clathrates for the first time and reported their infrared spectra.

Experimental

All chemicals used were reagent grade (Merck) and used without further purification.

The clathrate M(daddn)$Ni(CN)_4$.benzene (M = Co, Ni or Cd) was prepared by adding one millimole of 1,12-diaminododecane and one millimole of $K_2Ni(CN)_4$ solution in 20 mL of water (heated to about 60 °C) to one millimole of MCl_2 solution in 20 mL of water saturated with benzene. The clathrates M(daddn)$Ni(CN)_4$.G (M = Co, Ni or Cd ; G = naphthalene, anthracene, phenanthrene or biphenyl) were prepared as follows: one millimole of 1,12-diaminododecane and one millimole of $K_2Ni(CN)_4$ solution in water (30 mL), one millimole of MCl_2 solution in water (20 mL) and two millimoles of naphthalene (or anthracene, phenanthrene, biphenyl) in ethanol (30 mL) were mixed and stirred for two days. The precipitate formed was filtered, washed with ethanol and ether, successively, and kept in a desiccator containing molecular sieves and saturated guest vapour.

The freshly prepared compounds were analysed for C, H and N with the following results (found %/calculated %).

$Co(C_{12}H_{28}N_2)Ni(CN)_4\ C_6H_6$:	C = 52.57/52.83, H = 6.49/6.85, N = 16.37/16.80
$Ni(C_{12}H_{28}N_2)Ni(CN)_4\ C_6H_6$:	C = 52.41/52.85, H = 6.43/6.85, N = 16.29/16.81
$Cd(C_{12}H_{28}N_2)Ni(CN)_4\ C_6H_6$:	C = 47.16/47.72, H = 5.85/6.19, N = 14.77/15.18
$Co(C_{12}H_{28}N_2)Ni(CN)_4\ C_{10}H_8$:	C = 57.14/56.75, H = 6.74/6.59, N = 15.01/15.27
$Ni(C_{12}H_{28}N_2)Ni(CN)_4\ C_{10}H_8$:	C = 57.31/56.77, H = 6.24/6.60, N = 15.13/15.28
$Cd(C_{12}H_{28}N_2)Ni(CN)_4\ C_{10}H_8$:	C = 52.47/51.72, H = 5.89/6.01, N = 13.35/13.92
$Co(C_{12}H_{28}N_2)Ni(CN)_4\ C_{14}H_{10}$ (Ant):	C = 60.67/60.02, H = 6.20/6.38, N = 14.23/13.99
$Ni(C_{12}H_{28}N_2)Ni(CN)_4\ C_{14}H_{10}$ (Ant):	C = 60.49/60.04, H = 6.73/6.38, N = 14.41/14.00
$Cd(C_{12}H_{28}N_2)Ni(CN)_4\ C_{14}H_{10}$ (Ant):	C = 55.53/55.11, H = 6.09/5.86, N = 13.27/12.85
$Co(C_{12}H_{28}N_2)Ni(CN)_4\ C_{14}H_{10}$ (Phe):	C = 60.93/60.02, H = 6.58/6.38, N = 14.30/13.99
$Ni(C_{12}H_{28}N_2)Ni(CN)_4\ C_{14}H_{10}$ (Phe):	C = 60.37/60.04, H = 6.85/6.38, N = 14.33/14.00
$Cd(C_{12}H_{28}N_2)Ni(CN)_4\ C_{14}H_{10}$ (Phe):	C = 55.64/55.11, H = 6.15/5.86, N = 13.18/12.85
$Co(C_{12}H_{28}N_2)Ni(CN)_4\ C_{12}H_{10}$:	C = 57.94/58.36, H = 6.27/6.65, N = 14.41/14.58
$Ni(C_{12}H_{28}N_2)Ni(CN)_4\ C_{12}H_{10}$:	C = 58.21/58.38, H = 5.98/6.65, N = 14.29/14.59
$Cd(C_{12}H_{28}N_2)Ni(CN)_4\ C_{12}H_{10}$:	C = 52.96/53.40, H = 5.71/6.08, N = 13.08/13.34

The infrared spectra were recorded between 4000 – 400 cm^{-1} on a Mattson 1000 FTIR spectrometer, which was

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Table 1. The vibrational wavenumbers (cm^{-1}) of 1,12-diaminododecane in the M—Ni—G (M = Co, Ni or Cd, G = benzene, naphthalene, anthracene, phenanthrene or biphenyl)

Assignment[a]	daddn in CCl_4	Co—Ni—Bz	Ni—Ni—Bz	Cd—Ni—Bz	Co—Ni—Np	Ni—Ni—Np	Cd—Ni—Np	Co—Ni—Ant
$\nu_a(NH_2)$	3364m	3340m	3342m	3344m	3346m	3344m	3336m	3342m
$\nu_s(NH_2)$	3330s	3284m	3286m	3286m	3290m	3290m	3286m	3288m
$\nu_a(CH_2)$	2920vs	2924vs	2922vs	2922vs	2930vs	2932vs	2928vs	2927vs
$\nu_s(CH_2)$	2849vs	2848vs	2850vs	2852vs	2852vs	2854vs	2850vs	2852vs
$\delta(NH_2)$	1605w,sh	1603w,sh	1603w,sh	1603w,sh	no	no	no	no
$\delta(NH_2)$	1578vs	1585vs	1589vs	1585vs	1587vs	1586vs	1586vs	1598vs
$\delta(CH_2)$	1490m,sh	1495w	1495w	1495w	1495vw	1494vw	no	1496vw
$\delta(CH_2)$	1464s	1468s	1468s	1470s	1471s	1470s	1471s	1466m
$\delta(CH_2)$	1437w	1437vw	1439w	1439w	1441vw	1440vw	1440vw	1446w
$\rho_w(CH_2)$	1393w	1396vw	1396vw	1394vw	no	no	no	1396vw
$\rho_w(CH_2)$	1367w	1381vw	1377vw	1381vw	no	no	no	1381vw
$\rho_t(CH_2)$	1346w	1356vw	1356vw	1356vw	1354vw	1354vw	1356vw	1354w
$\rho_t(CH_2)$	1321vw	1340vw	1321vw	1342vw	1342vw	1342vw	1342vw	no
$\rho_t(NH_2)$	1302w	1300vw	1300vw	1300vw	1306vw	1306vw	1307vw	1313vw
$\nu(CN)$	1098w	1113m	1112m	1105m	1109vw	1109vw	1110vw	1113m
$\nu(CN)$	1065s	no	1082vw	1080vw	1083w	1086w	1085w	no
$\nu(CN)$	1061s	1062w	1063w	1059m	1059m	1061m	1060m	1063w
$\nu(CC)$	1020w	1030s	1032s	1024s	1032w	1032w	1030w	1032m
$\rho_w(NH_2)$	1004m	no	1011vw	no	999vw	1001vw	1000vw	997m
$\rho_w(NH_2)$	982s	982w	982w	984w	978vw	980vw	978vw	985vw
$\rho_w(NH_2)$	934w	935vw	937vw	no	935vw	935vw	935vw	no
$\rho_w(NH_2)$	913s	no	no	no	918vw	918vw	918vw	no
$\rho_r(CH_2)$	897s	891vw	895vw	893vw	no	no	no	no
$\rho_r(CH_2)$	819w	no	822vw	827vw	823vw	823vw	822vw	no
$\rho_r(CH_2)$	731m	735m	735m	735m	739w	737w,sh	731m	737m
$\rho_r(CH_2)$	722s	725m	725m	727m	725w	725w	725w	727m
δ(skeletal)	480w	561m	582m	540m	550m	577m	552m	557m

Assignment[a]	Ni—Ni—Ant	Cd—Ni—Ant	Co—Ni—Phe	Ni—Ni—Phe	Cd—Ni—Phe	Co—Ni—Bp	Ni—Ni—Bp	Cd—Ni—Bp
$\nu_a(NH_2)$	3346m	3346m	3344m	3347m	3349m	3346m	3348m	3350m
$\nu_s(NH_2)$	3290m	3288m	3288m	3291m	3291m	3288s	3290s	3292s
$\nu_a(CH_2)$	2927vs	2927vs	2929vs	2931vs	2928vs	2929vs	2931vs	2927vs
$\nu_s(CH_2)$	2852vs	2852vs	2852vs	2853vs	2852vs	2854vs	2854vs	2850vs
$\delta(NH_2)$	no	no	no	no	no	no	no	no
$\delta(NH_2)$	1598vs	1587vs	1590vs	1589vs	1586vs	1589vs	1591vs	1587vs
$\delta(CH_2)$	1498vw	1497vw	no	no	no	1495vvw	1495vvw	1495vw
$\delta(CH_2)$	1466m	1469m	1471m	1471m	1470m	1470s	1470s	1470s
$\delta(CH_2)$	1447w	1446w	no	no	no	no	no	no
$\rho_w(CH_2)$	1396vw	1394vw	no	no	no	1390vw	1396vw	1396vw
$\rho_w(CH_2)$	1381vw	1381vw	no	no	no	1381vw	1381vw	1378vw
$\rho_t(CH_2)$	1354w	1354w	1355w	1355w	1353w	1354vw	1355vw	1355vw
$\rho_t(CH_2)$	no	no	no	no	no	1340vw	1340vw	1340vw
$\rho_t(NH_2)$	1311vw	1313vw	no	no	no	1313vw	1311vw	1313vw
$\nu(CN)$	1113m	1107m	1115m	1115m	1106m	1113m	1115m	1108m
$\nu(CN)$	1082vw	no	no	no	no	no	no	no
$\nu(CN)$	1063w	1063w	1065w	1065w	1063w	1065w	1065w	1063w
$\nu(CC)$	1032m	1026m	1033m	1035m	1027m	1032m	1034m	1028m
$\rho_w(NH_2)$	999m	997m	no	1012m	1000w	no	no	no
$\rho_w(NH_2)$	984w	987vw	965m	986w	962m	987w	987w	987w
$\rho_w(NH_2)$	no	no	932vw	940w	932vw	931vw	932vw	932vw
$\rho_w(NH_2)$	no	no	no	no	no	no	no	no
$\rho_r(CH_2)$	no	no	896vw	894vw	891vw	895vw	891vw	895vw
$\rho_r(CH_2)$	no	no	no	no	no	no	no	no
$\rho_r(CH_2)$	737m	737m	741m	742m	742m	733m,sh	732m,sh	733m,sh
$\rho_r(CH_2)$	727m	728m	734m	733m	735m	no	no	no
δ(skeletal)	579m	537m	547m	580m	537m	557m	580m	538m

[a]Taken From Ref. [8]. v = very, s = strong, m = medium, w = weak, and sh = shoulder, no = not observed.

Table 2. The vibrational wavenumbers (cm^{-1}) of the $Ni(CN)_4$ group for the M—Ni—G (M = Co , Ni or Cd; G = benzene, naphthalene, anthracene, phenanthrene or biphenyl) clathrates

Assignment[a]	$Na_2Ni(CN)_4$[a]	Co—Ni—Bz	Ni—Ni—Bz	Cd—Ni—Bz	Co—Ni—Np	Ni—Ni—Np	Cd—Ni—Np	Co—Ni—Ant
ν_8(CN), Eu	2132	2158vs	2160vs	2148vs	2160vs	2164vs	2148vs	2154vs
Hot Band?	2128	2129	2135	no	no	no	no	2127
ν_9(NiC), Eu	543	530vw	532vw	525vw 515vw	511vw	511vw	530vw	
π(NiC), A_{2u}	448	451vw	453vw	445vw	455vw	459vw	457vw	453vw
δ(NiCN), Eu	433	434vs	436vs	424vs	434vs	438vs	424vs	432vs
Assignment[a]	Ni—Ni—Ant	Cd—Ni—Ant	Co—Ni—Phe	Ni—Ni—Phe	Cd—Ni—Phe	Co—Ni—Bp	Ni—Ni—Bp	Cd—Ni—Bp
ν_8(CN), Eu	2158vs	2146vs	2154vs	2159vs	2147vs	2152vs	2158vs	2148vs
Hot Band?	2131	no	no	no	2131	2129	2129	no
ν_9(NiC), Eu	no	no	no	no	542w	530vw	550vw	523vw
π(NiC), A_{2u}	455vw	no	no	no	no	453vw	455vw	445vw
δ(NiCN), Eu	436vs	424vs	434vs	437vs	425vs	434vs	436vs	424vs

[a]Taken From Ref. [9]. v = very, s = strong, m = medium, w = weak, and sh = shoulder, no = not observed.

Table 3. The vibrational wavenumbers (cm^{-1}) of benzene in the M—Ni—Bz (M = Co, Ni or Cd) clathrates

Assignment[a]	Liquid benzene[b]	Co—Ni—Bz	Ni—Ni—Bz	Cd—Ni—Bz
ν_{20} E_{1u}	3073	3086m	3086m	3086m
$\nu_8 + \nu_{19}$, E_{1u}	3075	3068w	3066w	3066w
ν_{13} B_{1u}	3048	3056m	3055m	3055m
$\nu_5 + \nu_{17}$ E_{1u}	1955	1957vw	1957vw	1959vw
$\nu_{10} + \nu_{17}$ E_{1u}	1815	1813w	1811w	1815w
ν_{19} E_{1u}	1479	1478m	1478m	1478m
ν_{14} B_{2u}	1309	1309w,sh	1309w,sh	1311w,sh
ν_{15} B_{2u}	1149	1157vw	1153vw	1151vw
ν_{18} E_{1u}	1036	1038m,sh	1036m,sh	1038m,sh
ν_{17} E_{2u}	966[a]	962m	968m	960m
ν_{11} A_{2u}	670	694s	694s	694s
		681vs	681vs	681vs

[a]Taken From Ref. [10]. [b]Taken From Ref. [11]. v = very, s = strong, m = medium, w = weak, and sh = shoulder.

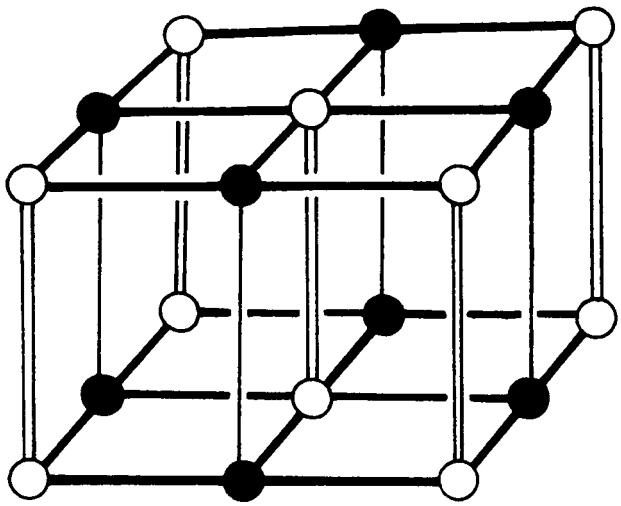

Figure 1. The model of the Hofmann-type host structure. Open circle: 6-coordinate M; solid circle: square-planar Ni; open column: an ambident ligand; thick line: CN bridged; thin line: edge of cavity.

calibrated using an indene/camphor/cyclohexane standard solution. The samples were prepared as mulls in nujol and poly(chlorotrifluoroethylene) between KBr plates.

Results and discussion

The infrared (IR) spectra of the host moities in the compounds M—Ni—G (M = Co, Ni or Cd; G = benzene, naphthalene, anthracene, phenanthrene or biphenyl) are found to be very similar. These similarities suggest that they also have similar structural features and the degree of interactions of the guest molecules, *daddn* ligand 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 [3–7]. The vibrational wavenumbers of the bands in the spectra of these species are tabulated in Tables 1–7, respectively, together with some relevant spectral data for comparison.

Table 4. The vibrational wavenumbers (cm^{-1}) of naphthalene in the M—Ni—Np (M = Co, Ni or Cd) clathrates

Assignment[a]	Naphthalene (in CCl_4 and CS_2[a])	Co—Ni—Np	Ni—Ni—Np	Cd—Ni—Np
ν_{41}, B_{3u}	3072	3068w	3068w	3068w
		3051w	3051w	
ν_{29}, B_{2u}	3014	3012vw	3013vw	3013vw
ν_{42}, B_{3u}	2976	2980m	2981m	2979m
ν_{30}, B_{2u}	2947	2962vw	2959vw	2959vw
ν_{43}, B_{3u}	1680	1672vw	1672vw	no
ν_{31}, B_{2u}	1595	1595s	1597s	1595s,sh
ν_{44}, B_{3u}	1510	1508m	1508m	1510m
ν_{32}, B_{2u}	1387	1389w	1389w	1387w
ν_{33}, B_{2u}	1268	1267m	1267m	1269m
ν_{45}, B_{3u}	1211	1211m	1211m	no
ν_{34}, B_{2u}	1139	1128m	1128m	1128m
ν_{46}, B_{3u}	1012	1011w	1011w	1009w
ν_{22}, B_{1u}	957	957m	957m	958m
ν_{47}, B_{3u}	876	891vw	891vw	893vw
ν_{23}, B_{1u}782	791vs	791vs	791vs	781vs
		782vs	782vs	782vs
ν_{35}, B_{2u}	752	750vw	750vw	750vw
ν_{48}, B_{3u}	618	619w	619w	619w
ν_{24}, B_{1u}	475	476s	476s	476s

[a]Taken from Ref. [12]. [b]Calculated value, taken from Ref. [12]. v = very, s = strong, m = medium, w = weak, and sh = shoulder, no = not observed.

Table 5. The vibrational wavenumbers (cm^{-1}) of anthracene in the M—Ni—Ant (M = Co, Ni or Cd) clathrates

Assignment[a]	Anthracene[a] (theory)	Anthracene[a] (in matrix)	Co—Ni— Ant	Ni—Ni—Ant	Cd—Ni—Ant
b_{2u}	3078m	3067–3068m	3087vw	3089vw	3086vw
b_{1u}	3063m	3055–3062m	3047m	3047m	3041m
b_{1u}	3044w	3032w	3022vw	3022vw	3020vw
b_{1u}	3039w	3017–3022w	3008vw	3006vw	3003vw
b_{1u}	1620w	1627w	1620vs	1620vs	1618vs
b_{2u}	1534w	1540–1542w	1533m	1533m	1533m
b_{1u}	1456w	1450w	1487vw	1487vw	1487vw
b_{2u}	1455w	1460w	1429w	1429w	1431w
b_{2u}	1343w	1346vw	1375w	1375w	1373w
b_{1u}	1311w	1318w	no	no	no
b_{1u}	1275w	1272w	1271w	1267w	1271w
b_{2u}	1169w	1167–1169vw	1182w	1198w	1198w
b_{2u}	1158w	–	1167w	1167w	1167w
b_{1u}	1156w	1149–1151w	1146m	1147m	1146m
b_{2u}	1001w	1001w	no	no	no
b_{3u}	962w	955–958w	964s	966s	962s
b_{1u}	908w	908vw	906w	904w	906w
b_{3u}	885s	878s	872s	872s	876s
b_{3u}	730vs	726–729vs	727vs	727vs	727vs
b_{2u}	613w	603w	602w	602w	602w
b_{3u}	471m	468–470m	465s	465s	467s

[a]Taken From Ref. [13]. v = very, s = strong, m = medium, w = weak, and sh = shoulder, no = not observed.

Table 6. The vibrational wavenumbers (cm^{-1}) of phenanthrene in the M—Ni—Phe (M = Co, Ni or Cd) clathrates

Assignment[a]	Phenanthrene[a] (theory)	Phenanthrene[a] (gas phase)	Co—Ni—Phe	Ni—Ni—Phe	Cd—Ni—Phe
a_1	3093s	–	no	no	no
b_2	3082s	–	no	no	no
b_2	3071s	–	no	no	no
a_1	3064s	3061vs	no	no	no
a_1	3057m	–	3051vw	3056vw	3056vw
a_1	3045w	–	no	3048vw	3046vw
a_1	1595w	1602w	1593m	1587m	1587m
b_2	1497w	1496w	1497vw	1496vw	1498vw
b_2	1462w	1452m	no	1469s	1466s
a_1	1444w	–	no	no	no
a_1	1250w	1239w	1247w	1240m	1241m
b_2	1038w	1032m	1035m	1041m	1038m
b_1	950w	940 –998w	964s	962s	948w
b_1	871m	859m	868w	863m	866w
b_1	817s	806s	816m	811s	812s
b_1	737vs	729vs	734vs	733vs	735vs
b_2	628w	615w	617w	617w	617w
b_1	498w	486w	502w	494w	494w
b_1	431w	–	no	no	no

[a]Taken from Ref. [13]. v = very, s = strong, m = medium, w = weak, and sh = shoulder, no = not observed.

Table 7. The vibrational wavenumbers (cm^{-1}) of biphenyl in the M—Ni—Bp (M = Co, Ni or Cd) clathrates

Assignment[a]	Biphenyl (in CCl_4 and CS_2[a])	Co—Ni—Bp	Ni—Ni—Bp	Cd—Ni—Bp
ν_1, B_{3u}	3080[b]	3082w	3082w	3080w
ν_2, B_{3u}	3072[b]	3066vw	3068vw	3066vw
ν_{12}, B_{2u}	3069[b]	3041vw	3041vw	3041vw
ν_{13}, B_{2u}	3068[b]	3024vw	3024vw	3022vw
ν_4, B_{3u}	1597	1595w,sh	1599w,sh	1595w,sh
ν_{14}, B_{2u}	1570	1568m	1568m	1566m
ν_5, B_{3u}	1482	1479s	1479s	1479s
ν_{15}, B_{2u}	1432	1431m	1431m	1433m
ν_{16}, B_{2u}	1383	no	no	no
ν_{17}, B_{2u}	1283	no	no	no
ν_6, B_{3u}	1176	1180vw	1180vw	1180vw
ν_{18}, B_{2u}	1156	1159vw	1159vw	1159vw
ν_{19}, B_{2u}	1074	1076vw	1076vw	1073vw
ν_7, B_{3u}	1040	1041w,sh	1043w,sh	1040w,sh
ν_8, B_{3u}	1008	1009vw	1011vw	1009vw
ν_9, B_{3u}	965	964s	968s	960s
ν_{23}, B_{1u}	903	906w	906w	906w
ν_{24}, B_{1u}	736	741s	741s	741s
ν_{25}, B_{1u}	698	700s	700s	700s
ν_{19}, B_{2u}	626	no	no	no
ν_{10}, B_{3u}	609	607w	607w	607w
ν_{26}, B_{1u}	484	no	484vw	no

[a]Taken from Ref. [14]. [b]Calculated value, taken from Ref. [13]. v = very, s = strong, m = medium, w = weak, and sh = shoulder, no = not observed.

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 1, together with the spectral data for *daddn* in solution in CCl_4.

The bands observed in the range of 3350–3284 cm^{-1} (Table 1) assigned to the NH_2 stretching frequencies, which are lower than the corresponding values of the free *daddn* molecule, are characteristic of a coordinated —NH_2 group. The absence of the splitting of the symmetric and asymmetric N—H bands of NH_2 groups suggests 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 $Ni(CN)_4$ 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 $Na_2Ni(CN)_4$ [9]. The structural studies on these salts have shown that the $Ni(CN)_4^{2-}$ ion is not coordinated to the cations [9]. 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 2 together with the vibrational wavenumbers of $K_2Ni(CN)_4$.

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 2). Such frequency shifts have been observed for other Hofmann-type clathrates, [7], 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 [3–7]. It follows that the N— ends of $Ni(CN)_4$ units are also bound to a 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 [3–7] suggesting that coordination about the Ni atom is square planar and the $[M\text{-}Ni(CN)]_\infty$ 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 = benzene, naphthalene, anthracene, phenanthrene or biphenyl) compounds are given in Tables 3–7, respectively, together with the wavenumbers of the free guest molecule on which the assignments are based. The assignments of the infrared spectra of the guest molecules in the clathrate compounds are based on the studies of Wilson [10], Painter and Koening [11], Lippincott and O'Reilly [12], Langhoff [13] and Zerbi and Sandroni [14], respectively. Our band assignments of the guest molecules in the compounds are in agreement with those given in the literature [10–14]. The IR spectral data of the compounds under study suggest that the guest molecules retain the free molecule symmetry. The most outstanding spectral features are the following.

The CH out-of-plane (ν_{11}, A_{2u}) vibrational band in the infrared spectra of the benzene compounds M—Ni—Bz (M = Co, Ni or Cd) (Table 3), is found to be shifted to higher frequency from that of liquid benzene and appears as a doublet. Similar positive shifts and a doublet [15] or a triplet splitting [16] were observed for Hofmann-type [3–7] and T_d-type [15, 16] clathrates. This upward shift was explained by weak hydrogen bonding between π electrons located above and below the plane of the benzene ring and the *daddn* molecule of the host lattice [3–7, 15, 16]. In the case of clathrates with triplet or doublet features, splittings have been ascribed to crystal field effects (strong host–guest interactions) [7, 16]. The shift in the CH out-of-plane vibrational band in naphthalene (ν_{23}, B_{1u}, 782 cm^{-1}), anthracene ($B3_{3u}$, 726 cm^{-1}) phenanthrene (B_1, 729 cm^{-1}) and biphenyl (ν_{24}, B_{1u}, 736 cm^{-1}) guests (Tables 4–7) is smaller than that of guest benzene. This may be due to weaker hydrogen bonding between the π electrons of the guest molecules and the large ligand *daddn* molecules (steric effect). Several modes of the naphthalene, phenanthrene or biphenyl molecules (Tables 4, 6, 7) have upward shifts in frequency compared to those in the free guest molecules. These shifts may also be due to weak hydrogen bonding between the guest and the ligand molecules.

The preceeding discussion considered together leads us to the conclusion that the compounds $M(daddn)Ni(CN)_4.G$ (M = Co, Ni or Cd; G = benzene, naphthalene, anthracene, phenanthrene or biphenyl) are similar in structure to the other Hofmann-diam-type clathrates.

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