Infrared Spectroscopic Study on the Hofmann-dadn-type and the T_d-dahxn-type Clathrates

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Abstract

Infrared spectra of $M(1,10\text{-diaminodecane})Ni(CN)_4 \cdot 1,5$ G (M = Co, Ni or Cd; G = o-xylene, m-xylene, p-xylene) and $Cd(1,6\text{-diaminohexane})M(CN)_4 \cdot C_6H_6$ (M = Cd or Hg) clathrates are reported. The 1,10-diaminodecane and 1,6-diaminohexane molecules in the host permit the inclusion of bulky guest molecules. The spectral data of clathrates were compared with those of the corresponding host. The spectral features suggest that these compounds are similar in structure to other Hofmann-type and Hofmann-T_d type clathrates, respectively.

Introduction

The structures of Hofmann-type clathrates [$Ni(NH_3)_2$-$Ni(CN)_4 \cdot 2C_6H_6$] and related clathrates compounds [$MLM'(CN)_4 \cdot xG$ (M = Mn, Fe, Co, Ni, Cu, Zn or Cd, L = unidentate or ambidentate ligand molecules, M′ = Ni, Pd, Pt; G = aromatic guest; x = number of guest molecules)] have already been determined [1, 2]. These studies show that the host structures of clathrates consist of corrugated polymeric layers of $\{M–M'(CN)_4\}_\infty$ with the L ligand molecules bound to the metal (M).

The structures of Hofmann-T_d-type clathrates [$Cd(NH_3)_2M(CN)_4 \cdot 2C_6H_6$ (M = Cd or Hg)] have already been determined by single crystal X-ray diffraction methods [3–6]. In the host framework of these compounds, the M atom is tetrahedrally coordinated to the carbon atoms of the four cyanide groups, while the Cd atom is octahedrally surrounded by six nitrogen atoms, two are from the NH_3 molecules attached to the Cd atom in position *trans* to each other, the other four are from cyanide groups. The $Hg(CN)_4$ groups are linked by the $Cd(NH_3)_2$ moieties to form a three-dimensional network. This structure provides two kinds of cavities for the guest molecules, one α, is similar to the rectangular box in the Hofmann-type structure and the other β, the former cavity approximates to a rectangular box and the latter to a biprismatic cage, as has been illustrated in previous articles [1–6].

In the present work, nine new Hofmann-diam-type calthrates $M(dadn)Ni(CN)_4 \cdot 1,5G$ (M = Co, Ni or Cd; dadn = 1,10-diaminodecane; G = o-xylene, m-xylene, p-xylene) (abbreviated henceforth as M–Ni–G) and two

new Hofmann-td-diam-type benzene clathrates with the formula $Cd(dahxn)M(CN)_4 \cdot C_6H_6$ (dahxn = l,6-diaminohexane, M = Cd or Hg) (abbreviated henceforth as Cd–M–Bz) have been prepared and their IR spectra are reported for the first time.

Experimental

The Hofmann-diam-type and Hofmann-t_d-diam-type clathrates were prepared according to the study reported previously [7, 8], respectively. The clathrates M–Ni–G (M = Co, Ni or Cd; G = o-xylene, m-xylene, p-xylene) were prepared by adding slightly more than 1 mmol of 1,10-diaminodecane in ethanol to a solution containing 1 mmol of $K_2Ni(CN)_4$, 1 mmol of MCl_2, 20 ml water saturated with the guest molecules. The clathrates Cd–Cd–Bz and. Cd–Hg–Bz were similar to that of $Cd(tn)M(CN)_4 \cdot 2C_6H_6$ (M = Cd or Hg) [8]: a solution composed of 1 mmol of $K_2M(CN)_4$ (M = Cd or Hg) and 1 mmol of 1,6-diaminohexane in water was added to a solution of $CdCl_2$ in water saturated benzene. The precipitate was filtered, washed with water, acetone and ether, successively, and kept in a desiccator containing saturated guest vapour.

IR spectra of the clathrate compounds were recorded in the range 4000–400 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 freshly prepared compounds were analyzed for C, H and N by a LECO CHNS-932 analyzer (found %/calculated %). The analytical results were agreement with the proposed formula.

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Compounds	C	H	N
$Co(NH_2(CH_2)_{10}NH_2) \cdot Ni(CN)_4 \cdot 1,5m - C_6H_4(CH_3)_2$	56,39/56,44	7,00/7,05	15,05/15,19
$Ni(NH_2(CH_2)_{10}NH_2) \cdot Ni(CN)_4 \cdot 1,5m - C_6H_4(CH_3)_2$	56,48/56,47	6,98/7,05	15,08/15,20
$Cd(NH_2(CH_2)_{10}NH_2) \cdot Ni(CN)_4 \cdot 1,5m - C_6H_4(CH_3)_2$	51,36/51,47	6,35/6,43	13,78/13,85
$Co(NH_2(CH_2)_{10}NH_2) \cdot Ni(CN)_4 \cdot 1,5o - C_6H_4(CH_3)_2$	56,42/56,44	7,01/7,05	15,14/15,19
$Ni(NH_2(CH_2)_{10}NH_2) \cdot Ni(CN)_4 \cdot 1,5o - C_6H_4(CH_3)_2$	56,42/56,47	7,00/7,05	15,14/15,20
$Cd(NH_2(CH_2)_{10}NH_2) \cdot Ni(CN)_4 \cdot 1,5o - C_6H_4(CH_3)_2$	51,40/51,47	6,40/6,43	13,79/13,85
$Co(NH_2(CH_2)_{10}NH_2) \cdot Ni(CN)_4 \cdot 1,5p - C_6H_4(CH_3)_2$	56,40/56,44	7,03/7,05	15,15/15,19
$Ni(NH_2(CH_2)_{10}NH_2) \cdot Ni(CN)_4 \cdot 1,5p - C_6H_4(CH_3)_2$	56,43/56,47	7,01/7,05	15,16/15,20
$Cd(NH_2(CH_2)_{10}NH_2) \cdot Ni(CN)_4 \cdot 1,5p - C_6H_4(CH_3)_2$	5,42/5,47	6,42/6,43	13,82/13,85
$Cd(NH_2(CH_2)_6NH_2)Cd(CN)_4 \cdot C_6H_6$	36,69/36,73	4,18/4,24	15,98/16,06
$Cd(NH_2(CH_2)_6NH_2)Hg(CN)_4 \cdot C_6H_6$	31,37/31,43	3,62/3,63	13,70/13,74

Results and discussion

The IR spectral features of the host moieties of the M–Ni–G (M = Co, Ni or Cd; G = o-xylene, m-xylene, p-xylene) and Cd–M–Bz (M = Cd or Hg) compounds are found to be similar to each other, suggesting that they have similar structural features also. These in turn suggest that the degrees of the interactions of the dadn or dahxn ligand, $Ni(CN)_4$ or $M(CN)_4$ (M = Cd or Hg) species and the aromatic guest molecules with their surroundings are almost the same for each compound and the symmetry restrictions of the compounds with different crystal symmetry possibilities are not effective.

It will be most favorable to divide the vibrations into three groups arising from the dadn ligands, from the $Ni(CN)_4$ units and from the guest moieties for the M–Ni–G clathrates, and from the dahxn ligands, from the $M(CN)_4$ (M = Cd or Hg) units and from the guest benzene moieties for the Cd–M–Bz clathrates.

M–Ni–G clathrates

The IR wavenumbers of the bands in the spectra for the M–Ni–G are tabulated in Tables 1–5 and for the Cd–M–G are tabulated in Tables 6–8, respectively, together with some relevant spectral data for comparison.

Up to the time of writing, there have been no studies concerning the spectral data for free dadn in metal complexes. Therefore, the assignments were made in terms of characteristic group frequencies. These assignments are given in Table 1, along with some relevant spectral data.

The N–H stretching frequencies of the dadn molecules in the M–Ni–G clathrates are found to be lower

Table 1. The vibrational wavenumbers (cm^{-1}) of 1,10-diaminodecane in the M–Ni–G (M = Co, Ni or Cd; G = m-xylene, o-xylene or p-xylene), m-x = m-xylene, o-x = o-xylene, p-x = p-xylene[a]

Assignment[b]	dadn in CCl_4[c]	Co–Ni–m-x	Ni–Ni–m-x	Cd–Ni–m-x	Co–Ni–o-x	Ni–Ni–o-x	Cd–Ni–o-x	Co–Ni–p-x	Ni–Ni–p-x	Cd–Ni–p-x
$v_a(NH_2)$	3386 s	3364 m	3350 m	3353 m	3364 s	3351 s	3353 s	3364 s	3349 s	3353 s
$v_s(NH_2)$	3329 s	3283 s	3283 s	3284 s	3281 s	3293 s	3296 s	3293 s	3292 s	3297 s
$v_a(CH_2)$	2927 vs	2922 vs	2922 vs	2924 vs	2923 vs	2923 vs	2925 vs	2924 vs	2924 vs	2924 vs
$v_s(CH_2)$	2854 vs	2850 vs	2852 vs	2851 vs	2852 vs	2852 vs	2853 vs	2853 vs	2852 vs	2853 vs
$\delta(NH_2)$	1610 s	1583 vs	1582 vs	1581 vs	1582 s	1585 s	1587 s	1583 s	1582 s	1586 s
$\delta(CH_2)$	1468 s	1467 s	1468 s	1467 s	1468 s	1470 s	1470 s	1469 s	1469 s	1469 s
$\delta(CH_2)$	1441 m,sh	1438 w	1441 vw	1440 vw	1441 w	1441 w	1438 w	1439 w	1441 w	1442 w
$\rho_w(CH_2)$	1389 m	1374 w	1382 w	1373 w	1384 w	1372 w	1382 w	1379 w	1379 w	1377 w
$\rho_w(CH_2)$	1363 vw	1358 vw	1357 vw	1357 vw	1357 vw	1357 vw	1357 vw	1357 vw	1357 vw	1355 vw
$\rho_t(CH_2)$	1319 w	1342 vw	1346 vw	1345 vw	1340 vw	1343 vw	1339 vw	1342 vw	1344 vw	1344 vw
$\rho_t(NH_2)$	1302 w	1307 w	1304 w	1309 w	1306 w	1307 w	1308 w	1307 w	1310 w	1307 w
$v(CN)$	1092 w,sh	1093 vw	1093 vw	1098 vw	1096 vw	1089 vw	1098 w	1107 vw	1098 vw	1096 w
$v(CN)$	1057 s	1062 w	1063 w	1065 vw	1059 vw	1060 vw	1061 vw	1058 m	1063 m	1058 m
$\rho_w(NH_2)$	1016 vw	1018 vw,sh	1019 vw,sh	1020 vw,sh	1038 vw,sh	1040 vw,sh	1049 vw,sh	1036 w,sh	1024 vw,sh	1044 m,sh
$\rho_r(CH_2)$	962 vw	995 s	1008 s	1004 s	995 s	1008 s	1002 s	997 s	1010 s	1001 s
$\rho_r(CH_2)$	820 m,br	847 w	843 w	840 w	846 vw	844 vw	847 vw	848 vw	841 vw	843 vw
$\rho_r(CH_2)$	721 w	740 w	740 w	737 w	734 w	734 w	738 vw	738 vw	737 vw	742 vw

[a]v, Very; s, strong; m, medium; w, weak; br, broad; sh, shoulder.
[b]Taken from Ref. [9].
[c]Taken from Ref. [7].

Table 2. The vibrational wave numbers (cm^{-1}) of cyanide group for the M–Ni–G (M = Co, Ni or Cd; G = *m*-xylene, *o*-xylene or *p*-xylene)[a]

Assignment[b]	Na$_2$Ni(CN)$_4$[b]	Co–Ni–*m*-x	Ni–Ni–*m*-x	Cd–Ni–*m*-x	Co–Ni–*o*-x	Ni–Ni–*o*-x	Cd–Ni–*o*-x	Co–Ni–*p*-x	Ni–Ni–*p*-x	Cd–Ni–*p*-x
v_8(CN),E$_u$	2132	2160 vs	2167 vs	2146 vs	2162 vs	2168 vs	2148 vs	2159 vs	2163 vs	2148 vs
	2128									2128 vw
v_9(NiC),E$_u$	543	503 vw	500 vw	500 vw	499 vw	499 vw	502 vw	503 vw	502 vw	505 vw
π(NiC),A$_{2u}$	448	456 vw	457 vw	456 vw	456 vw	457 vw	455 vw	454 vw	454 vw	455 vw
δ(NiCN),E$_u$	433	437 vs	438 vs	424 vs	437 vs	438 vs	423 vs	437 vs	438 vs	424 vs

[a]v, Very; s, strong; m, medium; w, weak; br, broad.
[b]Taken from Ref. [11].

than those of dadn in the CCl$_4$ (Table 1). These downward frequency shifts may be explained as weakening of the N–H bonds resulting from the electron draining from the N atom on account of its coordination to the metal atom M (Co, Ni or Cd) in the M–Ni–G. The ρ_w(NH$_2$) vibrational band in the infrared spectra of clathrates M–Ni–1,5G (M = Co, Ni or Cd; G = *o*-xylene, *m*-xylene, *p*-xylene) (Table 1), is found to be shifted to higher frequency from that of dadn molecule in the CCl$_4$. Similar positive shifts were observed for Hofmann type [10] clathrates. This upward shift was explained by weak hydrogen bonding between the guest molecule and the dadn ligand molecule.

In assigning the bands due to the Ni(CN)$_4^{2-}$ ion in the spectra of the compounds in the M–Ni–G clathrates, we refer to the work McCullough *et al.* [11] who presented vibrational data for the ion Ni(CN)$_4$ in Na$_2$Ni(CN)$_4$.

Vibrational data for Ni(CN)$_4$ groups in the compounds under are given in Table 2, together with the vibrational wavenumbers of Na$_2$Ni(CN)$_4$. The assigned wavenumbers for Ni(CN)$_4$ group in the compounds studied appear to be much higher than those for isolated Ni(CN)$_4$ units (Table 2). Such frequency shifts were observed for other Hofmann-diam-type [12, 13] and Hofmann-type [10] clathrates in which both ends of the CN group were coordinated and explained as the mechanical coupling of the internal modes of Ni(CN)$_4$ with the metal M–NC vibrations [10, 12, 13]. The characteristic frequencies of the Ni(CN)$_4$ group are found to be similar to those of the Hofmann-type clathrates, suggesting that coordination around Ni atom is square, and that [M–Ni(CN)]$_\infty$ layers have been conserved.

The assignment and the wavenumbers of the bands arising from the guest G molecule (G = *m*-xylene, *o*-xylene or *p*-xylene) in the IR spectra of our M–Ni–G compounds are given in Tables 3–5, respectively,

Table 3. The vibrational wavenumbers (cm^{-1}) of *m*-xylene in M–Ni–*m*-x (M = Co, Ni or Cd)[a]

Assignment[b]	*m*-xylene[b]	Co–Ni–*m*-x	Ni–Ni–*m*-x	Cd–Ni–*m*-x
v(CH),B$_2$	3052	3053 vw	3059 vw	3061 vw
v(CH),A$_1$	3032	3034 vw	3037 vw	3036 vw
v(CC),B$_2$	1613	1617 w	1617 w	1614 w
v(CC),A$_1$	1595	1601 w	1601 w	1598 w
v(CC),B$_2$	1492	1498 vw	1497 vw	1497 vw
v(CC),A$_1$	1460	n.o.	n.o.	n.o.
β(CH),B$_2$	1303	n.o.	n.o.	n.o.
α(CCC),B$_2$	1264	1281 vw	1280 vw	1277 vw
X-sens.,A$_1$	1252	1249 vw	1251 vw	1250 vw
β(CH),B$_2$	1167	1169 vw	1169 vw	1169 vw
X-sens.,B$_2$	1154	1155 w	1151 w	1151 w
β(CH),A$_1$	1094	1085 vw	1089 vw	1087 vw
γ(CH),B$_1$	968	960 vw	968 vw	964 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	769 vw	769 vw	769 vw
X-sens.,A$_1$	724	n.o.	n.o.	n.o.
π(CC),B$_1$	690	693 w	693 w	695 w
X-sens.,A$_1$	537	n.o.	n.o.	n.o.
X-sens.,B$_2$	515	520 vw	520 vw	522 vw
π(CC),B$_1$	433	432 vw	431 vw	432 vw
X-sens.,B$_2$	404	402 vw	402 vw	401 vw

[a]v, Very; s, strong; m, medium; w, weak; br, broad; sh, shoulder; n.o., not observed.
[b]Taken from Ref. [14].

Table 4. The vibrational wavenumbers (cm^{-1}) of *o*-xylene in M–Ni–*o*-x (M = Co, Ni or Cd)[a]

Assignment[b]	*o*-xylene[b]	Co–Ni–*o*-x	Ni–Ni–*o*-x	Cd–Ni–*o*-x
v(CH),B$_2$	3080	3106 w	3110 w	3106 vw
v(CH),A$_1$	3064	3080 w	3078 vw	3078 vw
v(CH),B$_2$	3048	3061 w	3057 vw	3058 vw
v(CC),A$_1$	1494	1509 w,sh	1510 w,sh	1510 w,sh
v(CC),B$_2$	1468	1497 m	1498 m	1496 m
Kekulé,A$_1$	1292	n.o.	n.o.	n.o.
β(CH),B$_2$	1290	1291 vw	1290 vw	1295 vw
X-sens.,A$_1$	1222	1221 vw	1222 w,sh	1221 vw
X-sens.,B$_2$	1185	1184 w	1183 w	1183 vw
β(CH),A$_1$	1155	1157 w	1162 w	1156 w
β(CH),B$_2$	1121	1119 w	1119 w	1119 w
β(CH),A$_1$	1052	1046 w,sh	1050 w,sh	1053 w
γ(CH),B$_1$	930	919 w	918 w	922 w
γ(CH),A$_2$	860	871 vw	867 w	866 w
X-sens.,B$_2$	826	826 vw	n.o.	n.o.
γ(CH),B$_1$	741	749 vs	751 vs	751 vs
X-sens.,A$_1$	581	595 vw	595 vw	592 vw
X-sens.,B$_2$	505	498 w	499 vw	500 vw
ϕ(CC),B$_1$	435	455 w,sh	455 w,sh	456 vw
X-sens B$_2$	406	403 vw	402 vw	401 vw

[a]v, Very; s, strong; m, medium; w, weak; br, broad; sh, shoulder; n.o., not observed.
[b]Taken from Ref. [15].

Table 5. The vibrational wave numbers (cm^{-1}) of *p*-xylene in the M–Ni–*p*-x (M = Co, Ni or Cd)[a]

Assignment[b]	Liquid *p*-xylene[b]	Co–Ni–G[c,d]	Co–Ni–*p*-x	Ni–Ni–*p*-x	Cd–Ni–*p*-x
v(CH),B$_{1u}$	3044	n.o	n.o.	3047 vw	3046 vw
v(CH),B$_{2u}$	3017	3018 vw	3018 vw	3021 vw	3023 vw
v(CH3),B$_{2u}$	2975	2985 w	2989 w	2990 w	2990 w
	2947	n.o.	n.o.	2948 vw, sh	2929 vw,sh
v(CH3),B$_{3u}$	2923	n.o.	n.o.	n.o.	n.o.
v(CC),B$_{1u}$	1529	1516 w	1516 w	1516 w	1516 w
δ(CH3),B$_{3u}$	1458	1475 w,sh	1477 w,sh	1475 w,sh	1475 w,sh
	1452	n.o.	n.o.	n.o.	n.o.
v(CC),B$_{2u}$	1421	1435 vw	1436 vw	1437 w	1437 w
δ(CH3),B$_{1u}$	1379	n.o.	n.o.	1366 w	1366 w
α(CCC),B$_{2u}$	1324	n.o.	n.o.	n.o.	n.o.
X-sens.,B$_{1u}$	1220	n.o.	n.o.	1216 vw	1206 vw
β(CH),B$_{2u}$	1120	1119 vw	1119 vw	1119 vw	1119 vw
τ(CH3),B$_{2u}$	1041	1049 m	1049 m	1048 w	1047 w
β(CH),B$_{1u}$	1023	1022 vw	1022 vw	1019 w	1019 w
γ(CH),B$_{3u}$	795	796 s	795 s	797 s	797 s
X-sens.,B$_{1u}$	725	729 m	729 m	726 m	725 m
ϕ(CC),B$_{3u}$	438	484 w	484 w	484 m	484 w

[a]v, Very; s, strong; m, medium; w, weak; br, broad; sh, shoulder; n.o., not observed.
[b]Taken from Ref. [16].
[c]Taken from Ref. [12].
[d]Co(1,8-diaminooctane)Ni(CN)4 · *p*-xylene.

Table 6. The vibrational wavenumbers (cm^{-1}) of 1,6-diaminohexane in the Cd–M–Bz (M = Cd or Hg) clathrates

Assignment[a]	dahxn in CCl$_4$[b]	Cd–Ni–Bz[c]	Cd–tn–Cd–2Bz[d]	Cd–dahxn–Cd–Bz	Cd–dahxn–Hg–Bz
v(NH$_2$)	3377 s	3348 s	3352 s	3350 s	3349 s
v(NH$_2$)	3286 s	3290 s	3295 s	3292 s	3292 s
v(CH$_2$)	2927vs	2924 vs	2970 s	2947 m	2944 m
				2922 m,sh	2920 m
v(CH$_2$)	2854 vs	2858 vs	2894 m	2886 m	2883 m
				2861 m	2853 m
δ(NH$_2$)	1578 s	1587 m	1586 s	1582 vs	1582 vs
δ(CH$_2$)	1485 s	1494 w	n.o.	1471 s	1478 s
δ(CH$_2$)	1437 w	1443 vw	1430 w	1447 w	1447 w
ρ_w(CH$_2$)	1389 w	1383 vw	1401 vw	1399 w	1397 w
ρ_w(CH$_2$)	1338 w	1336 vw	n.o.	1326 w	1329 w
ρ_t(NH$_2$)	1305 vw	n.o.	1298 vw	1271 w	1273 w
ρ_w(NH$_2$)	n.o.	n.o.	1093 m	n.o.	n.o.
v(CN)	1075 m	1080 m	1055 s	1064 m	1064 m
ρ_w(NH$_2$)	1052 vw	1062 w,sh	n.o.	1056 vw	1057 vw
?	n.o.	1014 m	n.o.	1011 m	1008 m
ρ_r(CH$_2$)	975 vw	964 m	986 vs	978 m	978 m
ρ_r(CH$_2$)	832 m,br ^{s}	858 vw	773 w	896 w	896 w
ρ_r(CH$_2$)	725 w	737 w	742 w	734 w	735 w

v, Very; s, strong; m, medium; vw, very weak; sh, shoulder; br, broad; n.o., not observed.
[a]Taken from Ref. [9].
[b]Taken from Ref. [13].
[c]Taken from Ref. [8].

together with the wavenumbers of the free guest molecule on which the assignments are based. The assignment of the bands of guest molecules in the IR spectra of the M–Ni–G clathrate compounds were based on the studies of Green [14–16]. Our spectra are found to be very similar in frequency and band pattern given by Green [14–16].

Several modes of the guest molecules have shifts in frequency compared to those in the free guest molecules. These shifts may occur due to the effect of weak hydrogen bonding [12]. These comparisons show that C$_{2v}$ symmetries are preserved for *m*-xylene, *o*-xylene or *p*-xylene molecules in M–Ni–G clathrates, respectively.

Table 7. The vibrational wavenumbers (cm^{-1}) of cyanide group for the Cd–M–Bz (M = Cd or Hg) clathrates

Assignment[a]	K$_2$Cd(CN)$_4$[a]	K$_2$Hg(CN)$_4$[a]	Cd–tn–Cd–Bz[b]	Cd–dahxn–Cd–Bz	Cd–dahxn–Hg–Bz
v_5(CN) F$_2$	2145	2146	2164 vs	2165 vs	2165 vs
v_6[v(MC) + δ(NCM)]F$_2$	316	330	348 s	353 s	355 s
v_7[v(MC) + δ(NCM)]F$_2$	250	235	263 w	268 w	270 w

[a]Taken from Ref. [21].
[b]Taken from Ref [8].

The decrease in the number of G molecules from 2 in Hofmann-type [1, 12, 17] and Hofmann-T$_d$-type [18] clathrates to 1,5 in the compounds studied is due to the fact that one of the four cavity units is occupied by the dadn ligands, and the other three cavity units of the host are occupied by the guest molecules. Host–guest interactions in the clathrate structure are not effective because of the bulkiness of dadn ligand molecules.

Cd–M–Bz Clathrates

The assignments and the wavenumbers of the vibration bands of the dahxn observed in the spectra of the Cd–M–Bz clathrate compounds under study are given in Table 6, together with the spectral data for dahxn in the liquid phase and in solution in CCl$_4$ on which the assignments are based [9]. The assignments were made in terms of characteristic group frequencies. Our assignments for the localized vibrations are in good agreement with those reported previously for Td-type Cd–tn–Cd–2Bz [8]. Some vibration bands of the ligand molecule

show upward or downwards shifts when compared to the same vibrations (for example, the band observed in the 3350–3292 cm^{-1} assigned to the NH$_2$ symmetric and asymmetric stretching frequencies) in the pure ligands as shown in Table 6. Similar observations were also reported for different clathrates [18, 19]. It shows that the ligand molecules are bound directly to the metal M (M = Cd or Hg). Considering the present spectral data it is not possible to give an account on the conformation of the dahxn ligand in our compounds. However, some implication may be deduced from the Cd(dahxn)Ni(CN)$_4$·G in all *trans* conformation [9, 20]. Therefore the flexible dahxn molecule is also expected to be in *trans* form in the Cd–M–Bz compounds.

The infrared data for M(CN)$_4$ groups in the compounds under study are given in Table 7, together with the infrared wavenumbers of K$_2$Cd(CN)$_4$ [22] and K$_2$Hg(CN)$_4$ [23] and in the clathrate Cd–tn–Cd–2Bz [8] for comparison. The assigned wavenumbers for the M(CN)$_4$ groups in the compounds studied appear to be much higher then those for M(CN)$_4$ element in

Table 8. The Infrared wavenumbers (cm^{-1}) of benzene in the Cd–M–Bz (M = Cd or Hg) clathrates

Assignment[a]	Liquid benzene[b]	Cd–dahxn–Ni–Bz[c]	Cd–tn–Cd–Bz[d]	Cd–dahxn–Cd–Bz	Cd–dahxn–Hg–Bz
v_{20}, E$_{1u}$	3073	3078 m	3083 m	3084 m	3084 m
$v_8 + v_{19}$	3075	3060 m	3064 m	3066 m	3065 m
v_{13}, B1u	3048	3022 s	3028 s	3031 m	3029 m
v_2, A$_{1g}$	n.o.		3064 m	3061 vw	3062 vw
v_7, E$_{2u}$	n.o.		n.o.	3043 vw	3045 vw
$v_5 + v_{17}$, E$_{1u}$	1955	1979 w	1969 w	1977 w	1980 w
$v_{10} + v_{17}$	1815	1830 w	1822 w	1836 w	1840 w
v_{19}, E$_{1u}$	1479	1474 m	1479 s	1478 s	1477 s
v_{14}, B$_{2u}$	1309	1309 vw	n.o.	1309 w	1310 w
v_9, E$_{2g}$	–		n.o.	1183 w	1183 w
v_{15}, B$_{2u}$	1149	1146 vw	1151 vw	1154 w	1155 w
v_{18}, E$_{1u}$	1036	1034 w	1035 m	1035 m	1035 m
v_5, B$_{2g}$	989	n.o.	n.o.	n.o.	n.o.
v_{17}, E$_{2u}$	966	n.o.	n.o.	n.o.	n.o.
v_{10}, E$_{1u}$	–	n.o.	n.o.	850 vw	850 vw
v_{11}, A$_{2u}$	670	690 vs	700 sh	693 vs	694 vs
		n.o.	688 vs	n.o.	n.o.
		n.o.	679 sh	n.o.	n.o.
v_6, E$_{2g}$	–	n.o.	n.o.	602 vw	604 vw

v, Very; s, strong; m, medium; w, weak; sh, shoulder; n.o., not observed.
[a]Taken from Ref. [27].
[b]Ir bands from Ref. [28].
[c]Taken from Ref. [13].
[d]Taken from Ref. [8].

$K_2M(CN)_4$ (M = Cd or Hg) (Table 7). Such frequency shifts have been observed for other T_d-type clathrates [8, 24, 25] and T_d-type complexes [26], in which both ends of the CN group are coordinated and explained as the mechanical coupling of the internal modes of $M(CN)_4$ (M = Cd or Hg) with the Cd–NC vibrations [8, 13, 24–26].

The assignment and the wavenumbers of the infrared bands of benzene observed in the spectra of the Cd–M–Bz clathrate compounds are given in Table 8, along with the wavenumbers of benzene in the liquid phase [28] and in the clathrate Cd–tn–Cd–2Bz [8] for comparison. The most structurally informative spectral features are the following.

The CH out-of-plane mode (A_{2u}) in the infrared spectra of the clathrates appears as a singlet (Table 8). This infrared mode also appears as a triplet for M(ethylenediamine)M′(CN)$_4$ · 2C$_6$H$_6$ (M = Mn or Cd; M′ = Cd or Hg) [18] and a doublet for M(NH$_3$)$_2$M′(CN)$_4$ · 2C$_6$H$_6$ (M = Mn or Cd; M′ = Cd or Hg) [24], and a singlet for Cd(4-4′-bipyridyl)M′(CN)$_4$ · 2C$_6$H$_6$ (M = Cd or Hg) [29]. In the case of clathrates with doublet and triplet features, the splitting is explained by the strong host–guest interaction (i.e. crystal field effect) [29]. In the case of clathrates with a single band, because of the larger cavities due to the ligands, the host–guest interactions are expected not to be effective for splitting [25].

Another feature of the CH out-of-plane (A_{2u}) infrared band is that it is found to be shifted to higher wavenumbers from that of liquid benzene (670 cm^{-1}). Similar positive shifts have been observed for Hofmann-type [30] and T_d-type clathrates [8, 13, 24, 29]. This upward shift was explained for the Hofmann-type clathrates [19] by the presence of a weak hydrogen bond between (electrons located above and below the plane of the benzene ring and the ammonia molecules of the host lattice.

It should be noted that, in our clathrates, the number of guest molecules is one. The decrease in the number of guest molecules from two in Hoffman-T_d-type [8, 24] to one in the present series is due to the fact that the α-cavities may be occupied by the dahxn molecules and

the β-cavities may be occupy by the guest molecule [9, 20]. A similar decrease has been found in the other Hofmann-diam-type clathrates [20, 30].

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