



Infrared Spectroscopic and Gravimetric Studies on the Dicyclohexylaminemetal(II) Tetracyanonickellate(II) Host-aromatic Guest Systems

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Abstract

$\text{Co}(\text{Cyclohexylamine})_2\text{Ni}(\text{CN})_4$ and $\text{Cd}(\text{Cyclohexylamine})_2\text{Ni}(\text{CN})_4$ host compounds have been prepared in powder form. The spectral data suggest that these complexes are similar in structure to the Hofmann-dma-type hosts. The sorption processes of the aromatic guests (benzene, toluene, *o*-, *m*-, *p*-xylene, naphthalene, 1,2-, 1,3-dichlorobenzene and 1,4-dibromobenzene) in these hosts have been examined at room temperature by gravimetric and spectroscopic measurements. The desorption of the benzene guest against time has been measured. The host structures change on inclusion of the guests and recover after liberation. The host complexes have been suggested as sorbents for isomeric separations.

Introduction

The inclusion of benzene molecules as a guest into a host framework has been used for the purification of benzene [1]. A patent has been obtained for the recovery of purified benzene from hydrocarbon stocks using Hofmann's clathrate, $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{Benzene}$, as the collector [2]. Based on the structure of this prototype clathrate several analogous compounds called Hofmann-type clathrates have been derived by appropriate replacements of the host moieties and the guest molecules [3]. These clathrates are designated with a general formula $\text{M}(\text{II})\text{L}_2\text{M}'(\text{II})(\text{CN})_4 \cdot n\text{G}$, where, M is Mn, Fe, Co, Ni, Cu, Zn or Cd; M' is Ni, Pd or Pt; L is a unidentate ligand molecule and *n* is the number of G (guest) molecules depending on the bulkiness of the ligands. The host framework consists of two dimensional polymeric layers composed of ML_2 cations and $\text{M}'(\text{CN})_4$ anions. The M' atoms are coordinated to four C atoms of the CN groups in a square-planar environment. M atoms are octahedrally surrounded by 6N atoms, four from the CN groups and the other two are from two ligand molecules. The ligand molecules lie above and below the layers. The layers and the ligands as blocking units provide empty spaces of varying shapes and dimensions, in which guest molecules may be imprisoned [3].

The host structure described above is not unique for the given chemical formula. A number of studies have suggested that similar compositions never support similar structures for the cyanometallate inclusion and complex systems [3, 4]. Among them, dimethylamine (dma) gives a number

of inclusion compounds with a selectivity very different from the Hofmann-type hosts mentioned above [3]. The host $\text{Cd}(\text{dma})_2\text{Ni}(\text{CN})_4$ can include beside benzene, toluene, xylenes, naphthalene, chlorobenzene, bromobenzene, dichlorobenzene, and *o*-, *p*- and *m*-toluidine, which have never been found enclathrated into Hofmann-type and analogous hosts. Some of these inclusion compounds show x-ray diffraction patterns characteristic of the intercalate structures of these guests between the layered metal complex sheets. The expanded spacing (in the range of 9.2–9.5 Å for toluene, chlorobenzene, bromobenzene, *p*-xylene and naphthalene) has been interpreted in terms of the guest molecules arranged between sheets covered with hydrophobic methyl groups which may form a tunnel-like cavity between the sheets.

These unusual results prompted us to explore the inclusion behaviours of the Hofmann-type and Hofmann- T_d -type hosts with a series of cycloalkylamines and a variety of guests different in size and shape from those enclathrated in the Hofmann-type and Hofmann- T_d -type hosts.

Now, for the first time, we have prepared two new Hofmann-dma-type host complexes, $\text{M}(\text{cyclohexylamine})_2\text{Ni}(\text{CN})_4$, (M=Co or Cd) (abbr. M-CHA-Ni,) in powder form. In this study, gravimetric and infrared spectroscopic measurements of the sorption processes of the aromatic guests (benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, 1,2-,1,3-,1,4-dichlorobenzene and naphthalene) in the vapour phase have been examined at room temperature. The loss of benzene from the host compounds against time has been measured.

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Experimental

All chemicals used were reagent grade and used without further purification.

Co-CHA-Ni (or Cd-CHA-Ni): this host complex was prepared by adding 9 millimoles of CHA in solution in ethanol (ca.20 mL) into 3 millimoles of the Hofmann-H₂O-type hydrate Co(H₂O)₂Ni(CN)₄(4H₂O) (0.9896 g) (or Cd(H₂O)₂Ni(CN)₄(4H₂O) (1.1498 g)) which was prepared by the procedure of Mathey and Mazieres [5]. The precipitate was filtered, washed with ethanol and ether, successively, and dried in air to constant weight. The complexes Co(CHA)₂Ni(CN)₄ and Cd(CHA)₂Ni(CN)₄ were obtained in quantitative yield. The freshly prepared complexes were analysed for Co, Cd, Ni, C, H and N with the following results (found %/calculated %): Co(C₆H₁₃N)₂Ni(CN)₄: Ni = 14.21/13.91, Co = 14.29/14.03, C = 47.22/45.75, H = 6.23/6.24, N = 20.27/20.01.

Cd(C₆H₁₃N)₂Ni(CN)₄: Ni = 12.57/12.39, Cd = 23.81/23.74, C = 42.75/40.59, H = 5.79/5.53, N = 18.00/17.75.

The clathrate compounds were prepared by leaving the host complexes in the saturated guest vapour as described below.

Infrared spectra of the compounds were recorded in the range 4000–400 cm⁻¹ on a Mattson 1000 FT-IR spectrometer which was calibrated using an indene/camphor/cyclohexane standard solution. The samples were prepared as mulls in Nujol and poly(chlorotrifluoroethylene) between CsI plates

Results and discussion

Before embarking upon the inclusion and liberation of the guest species in the host complexes, it is appropriate to elucidate the host structure on the basis of the available spectral data.

The infrared spectra of the host compounds are shown in Figure 1. The assignment and the wavenumbers of the fundamental vibrations arising from the Ni(CN)₄ and the CHA moieties are given in Tables 1 and 2, respectively. It will be convenient to divide the vibrations into two, arising from the Ni(CN)₄ unit and from the CHA ligand. The assignment of the spectral bands due to the Ni(CN)₄ moieties are straightforward, since these bands are persistent and picked out with ease [6–10].

Ni(CN)₄ group vibrations

The fact that in the host framework of the Hofmann-type clathrates [3–5, 7, 8] and Hofmann-type host complexes [6, 9, 10], the metal atom in Ni(CN)₄ is square planar and surrounded by the carbon ends of the CN ions suggests that the host framework of the complexes studied also have square planar Ni(CN)₄ units. In order to assign the bands attributable to the Ni(CN)₄ ion in the spectra, we refer to the work of McCullough *et al.* who presented vibrational data for the salt Na₂Ni(CN)₄ in the solid state [11]. In this salt the Ni(CN)₄

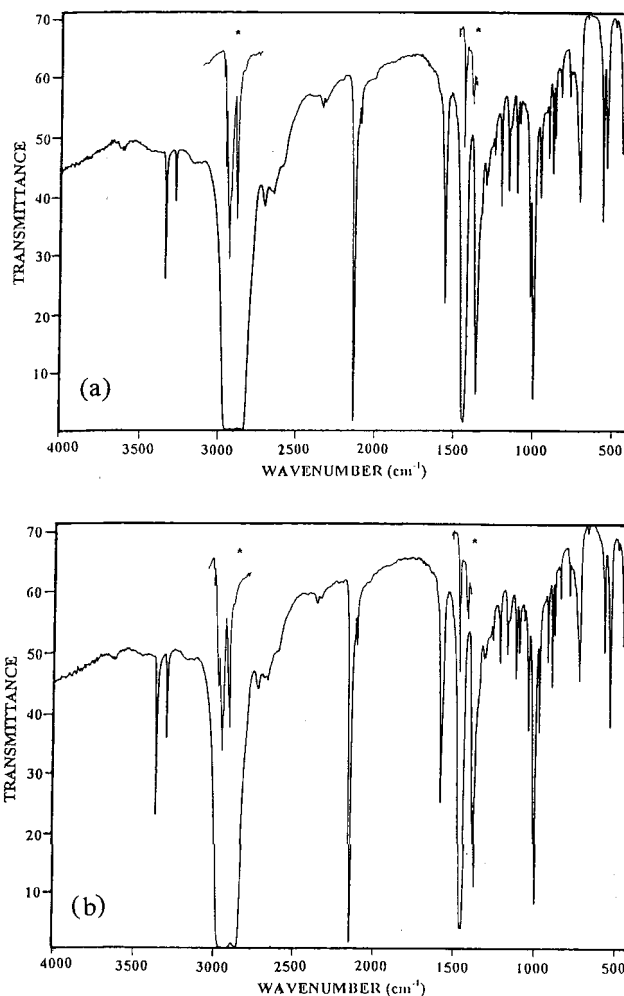


Figure 1. Spectra of Co-CHA-Ni (a) and Cd-CHA-Ni (b) host complexes in nujol and *poly(chlorotrifluoroethylene) – oil,

anion is not coordinated to Na⁺ ion; therefore, it can be treated as an isolated unit with D_{4h} symmetry and thus used as a reference to comment on vibrational changes when Co–NC (or Cd–NC) bonding takes place. The spectral data for Ni(CN)₄ groups in the host compounds are given in Table 1, together with spectral data of Na₂Ni(CN)₄. The assigned wavenumber of the Ni(CN)₄ units of the complexes studied appear to be much higher than those for the isolated Ni(CN)₄ ion (Table 1). Such frequency shifts have been observed for Hofmann-type host frameworks [6–10], and are attributed to the mechanical coupling of the internal modes of Ni(CN)₄ with the M–NC vibrations. It follows that the N-termini of the Ni(CN)₄ group are bound to a Co (or Cd) atom in the host compounds.

Cyclohexylamine vibrations

Up to the time of writing, there have been no reports of the vibrational spectra of the CHA molecule. Owing to the low symmetry of the CHA ligand molecule, the assignments of the CHA vibrational bands of the CHA ligand in the spectra were made in terms of the characteristic group frequencies. The tentative assignments of the fundamental bands of CHA observed in the spectra of the compounds under study are

Table 1. The wavenumbers of the Ni(CN)₄ unit of the M(CHA)₂Ni(CN)₄ complexes

| Assignment | Na ₂ Ni(CN) ₄ | Co-CHA-Ni | Cd-CHA-Ni | Co-CHA-NiG G = Benzene | Cd-CHA-Ni-2G G = Benzene | Co-CHA-Ni-2G G = Toluene | Cd-CHA-Ni-2G G = Toluene | Co-CHA-Ni-2G G = <i>o</i> -Xylene | Cd-CHA-Ni-2G G = <i>o</i> -Xylene |
|--------------------------------------|--|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|---|---|--------------------------------------|--------------------------------------|
| $\nu_8, \nu(\text{CN}), E_u$ | 2128 vs, 2132 vs | 2153 vs | 2147 vs | 2163 vs | 2160 | 2162 vs | 2151 vs | 2160 s, 2154 s | 2150 vs |
| Hot band | – | 2126 w | 2128 w | – | – | 2121 vw | no | 2121 vw | 2122 vw |
| $\nu(\text{C}_{13}\text{N})$ | 2087 w | 2112 w | 2108 w | 2123 w | 2122 | no | 2112 vw | 2111 vw | 2110 vw |
| $\nu_9, \nu(\text{NiC}), E_u$ | 543 w | – | – | – | – | no | no | no | no |
| $\nu_{12}, \pi(\text{NiCN}), A_{2u}$ | 488 w | 454 w | 449 w | 446 w | 445 | no | no | no | 446 w, sh |
| $\nu_{10}, \delta(\text{NiCN}), E_u$ | 427 vs | 432 vs | 425 vs | 437 vs | 425 vs | 436 vs | 423 vs | 435 vs | 424 vs |
| Assignment ^a | Na ₂ Ni(CN) ₄ ^a | Co-CHA-Ni-2G G = <i>m</i> -Xylene | Cd-CHA-Ni-2G G = <i>m</i> -Xylene | Co-CHA-Ni-2G G = <i>p</i> -Xylene | Cd-CHA-Ni-2G G = <i>p</i> -Xylene | Cd-CHA-Ni-2G G = 1,2-dichlorobenzene | Cd-CHA-Ni-2G G = 1,3-dichlorobenzene | Cd-CHA-Ni-2G G = Naphthalene | |
| $\nu_8, \nu(\text{CN}), E_u$ | 2128 vs, 2132 vs | 2161 s, 2152 s | 2161 s, 2153 m, sh | 2163 s, 2153 m, sh | 2156 s, 2147 m, sh | 2152 s, 2147 m, sh | 2149 s, 2144 m, sh | 2152 s, 2145 m, sh | |
| Hot band | – | 2124 vw | 2122 vw | 2124 vw | no | no | no | no | |
| $\nu(\text{C}_{13}\text{N})$ | 2087 w | 2113 vw | 2108 w | 2111 vw | 2112 vw | 2110 vw | 2110 vw | 2112 vw | |
| $\nu_{19}, \nu(\text{NiC}), E_u$ | 543 w | no | no | no | no | no | no | no | |
| $\nu_{12}, \pi(\text{NiCN}), A_{2u}$ | 488 w | 447 w, sh | 437 w, sh | 447 w, sh | 438 w, sh | 440 w, sh | 448 w, sh | no | |
| $\nu_{10}, \delta(\text{NiCN}), E_u$ | 427 vs | 425 vs | 422 vs | 424 vs | 424 vs | 423 vs | 422 vs | 423 vs | |

^aTaken from Ref. [11]. Abbr.: v = very, s = strong, m = medium, w = weak, sh = shoulder, no = not observed.

Table 2a. Assignment and the IR wavenumbers for the CHA in M-CHA-Ni complexes and their clathrates*

| Assignment | CHA (liquid) | | CHA in nujol and PCI-F-ethylene | | Co-CHA-Ni | | Cd-CHA-Ni | | Co-CHA-Ni-2G G = Benzene | | Cd-CHA-Ni-2G G = Benzene | | Co-CHA-Ni-2G G = Toluene | | Cd-CHA-Ni-2G G = Toluene | |
|------------------------------|--------------|-----------|------------------------------------|-----------|-------------|-----------|-------------|-----------|-----------------------------|-----------|-----------------------------|-----------|-----------------------------|-----------|-----------------------------|-----------|
| | Wavenumber | Intensity | Wavenumber | Intensity | Wavenumber | Intensity | Wavenumber | Intensity | Wavenumber | Intensity | Wavenumber | Intensity | Wavenumber | Intensity | Wavenumber | Intensity |
| NH ₂ antisym. str | 3353 m | | 3383 s | | 3350 s | | 3355 s | | 3329 s | | 3332 s | | 3341 s | | 3333 s | |
| NH ₂ sym. str | 3280 m | | 3320 m | | 3288 m | | 3292 m | | 3276 m | | 3277 m | | 3281 m | | 3275 m | |
| CH ₂ antisym. str | - | | - | | 2984 w | | 2971 w | | 2980 w | | 2972 w | | 2975 w | | 2972 w | |
| CH ₂ antisym. str | - | | - | | 2961 m, sh | | 2948 m, sh | | 2962 vw | | 2948 w, sh | | no | | 2949 m, sh | |
| CH ₂ antisym. str | - | | - | | 2939 w, sh | | 2939 w, sh | | 2937 w, sh | | 2937 w, sh | | no | | 2935 m, sh | |
| CH ₂ sym. str | 2926 vs | | 2934 vs | | 2926 ms | | 2920 ms | | 2923 vs | | 2919 vs | | 2927 ms | | 2920 ms | |
| CH ₂ sym. str | 2897 m, sh | | 2912 m, sh | | 2909 m, sh | | 2905 m, sh | | 2906 m, sh | | 2905 m, sh | | 2906 m, sh | | 2906 m, sh | |
| CH ₂ sym. str | - | | - | | 2887 w, sh | | 2888 w, sh | | 2889 w, sh | | 2888 w, sh | | no | | no | |
| CH str | 2853 ms | | 2858 ms | | 2858 ms | | 2850 ms | | 2852 vs | | 2851 vs | | 2852 ms | | 2851 ms | |
| NH ₂ scissoring | 1598 ms | | 1616 ms | | 1575 ms | | 1580 ms | | 1582 ms | | 1584 ms | | 1578 ms | | 1578 ms | |
| | 1568 w, sh | | 1574 w | | 1560 w, sh | | 1559 m, sh | | 1559 vw | | no | | 1560 w | | 1560 w | |
| CH ₂ deform. | - | | - | | 1466 w | | 1469 vw | | 1466 w | | 1464 w | | 1465 vw, sh | | 1465 vw, sh | |
| CH ₂ deform | 1449 ms | | 1453 ms | | 1452 ms | | 1452 ms | | 1451 vs | | 1451 vs | | 1450 ms | | 1452 ms | |
| CH ₂ deform | - | | - | | 1438 w, sh | | 1442 w, sh | | 1444 w, sh | | 1443 w, sh | | 1437 w, sh | | 1439 w, sh | |
| CH bending | 1377 m | | 1377 m | | 1378 w, sh | | 1387 w, sh | | 1389 w, sh | | 1389 w, sh | | 1389 w, sh | | 1388 w, sh | |
| | 1347 w | | - | | 1311 vw | | 1312 vw | | 1312 w | | 1310 w | | 1313 w | | 1313 w | |
| NH ₂ wagging | 1281 w, sh | | 1309 w | | 1303 vw, sh | | 1305 vw | | 1303 vw, sh | | 1304 vw, sh | | 1305 w | | 1305 w | |
| NH ₂ wagging | 1281 w | | - | | 1275 vw | | 1277 vw | | 1274 vw | | 1275 vw | | 1278 w | | 1277 w | |
| CH ₂ wagging | 1259 w | | 1259 w | | 1257 vw, sh | | 1257 vw, sh | | 1256 w | | 1256 w | | 1257 w | | 1257 w | |
| CH ₂ wagging | 1205 w | | 1203 w | | 1217 m | | 1213 m | | 1218 m | | 1215 m | | 1217 m | | 1214 m | |
| CH ₂ wagging | 1173 w | | 1170 w | | 1169 m | | 1169 m | | 1172 m | | 1170 m | | 1180 w | | 1169 m | |
| Ring-deform. | 1152 w | | 1148 w | | 1155 w, sh | | 1156 w, sh | | 1157 w, sh | | 1155 w, sh | | 1159 vw | | 1157 vw | |
| CH ₂ twisting | 1102 m | | 1105 m | | 1117 m | | 1114 m | | 1121 m | | 1117 m | | 1120 m | | 1116 m | |
| CH ₂ twisting | 1092 m | | 1090 m | | 1097 vw | | 1093 w | | 1090 vw | | 1097 w | | 1089 w | | 1093 w | |
| CH ₂ twisting | - | | 1061 vw | | 1063 vw | | 1062 vw | | 1064 w, sh | | 1063 w, sh | | 1069 w | | 1067 w | |
| C-N str | 1038 w | | 1036 m | | 1035 s | | 1036 s | | 1036 s | | 1039 s | | 1043 m | | 1040 m | |
| C-N str | - | | - | | 1014 vs | | 1000 vs | | 1027 m, sh | | 1016 vs | | 1021 ms | | 1030 ms | |
| Ring breathing | 978 m | | 975 w | | 968 s | | 968 s | | 968 s | | 965 s | | 968 m | | 967 s | |
| Ring breathing | - | | - | | 940 vw | | 938 vw | | no | | no | | 940 vw | | 941 vw | |
| NH ₂ twisting | 932 m | | 926 m | | 918 m | | 917 m | | 918 w | | 918 w | | 920 m | | 920 m | |
| Ring deformation | 898 | | 893 s | | 892 s | | 889 s | | 891 s | | 889 s | | 892 μ | | 890 m | |
| C-H bending | 862 m | | 860 w, sh | | 876 m | | 875 m | | 879 w | | 878 w | | 877 w | | 879 w | |
| CH ₂ rocking | 840 | | 843 | | 840 w | | 840 w | | 843 w | | 842 w | | 845 w | | 843 w | |
| CH ₂ rocking | 778 m | | 775 s | | 785 w | | 783 w | | 786 w | | 784 w | | 787 w | | 790 w | |
| Ring deformation | - | | - | | - | | - | | 772 vw | | 769 vw | | 771 vw | | 770 vw | |
| CH ₂ rocking | 600 vw | | - | | 595 w | | 592 vw | | 589 vw, sh | | 593 vw, sh | | no | | no | |
| CH ₂ rocking | - | | - | | 576 s | | 567 m | | 574 s | | 565 s | | 577 s | | 570 s | |
| CH ₂ rocking | 556 w | | 554 m | | 552 m | | 532 s | | 547 s | | 531 s | | 553 m | | 533 s | |
| Ring C-N bending | 464 w | | 466 w | | 491 w | | 480 w | | 490 vw | | 481 w | | 490 w | | 482 vw | |
| | - | | 452 w | | 454 w, sh | | 449 w, sh | | 448 w, sh | | 445 w, sh | | no | | 446 w, sh | |

* *p*(C13F Et)(poly(chloro-trifluoro ethylene)), v = very, s = strong, m = medium, w = weak, no = not observed.

Table 2b. Assignment and the IR wavenumbers for the CHA in the clathrates

| Assignment | Co-CHA-Ni-1,5G | | Cd-CHA-Ni-2G | | Co-CHA-Ni-2G | | Cd-CHA-Ni-1,5G | | Cd-CHA-Ni-G | | Cd-CHA-Ni-2G | | Cd-CHA-Ni-2G | |
|-------------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|-------------------------|-------------------------|-----------------|-----------------|--|
| | G = <i>o</i> -Xylene | G = <i>o</i> -Xylene | G = <i>o</i> -Xylene | G = <i>o</i> -Xylene | G = <i>m</i> -Xylene | G = <i>m</i> -Xylene | G = <i>m</i> -Xylene | G = <i>p</i> -Xylene | G = <i>p</i> -Xylene | G = 1,2-dichlorobenzene | G = 1,3-dichlorobenzene | G = Naphthalene | G = Naphthalene | |
| NH ₂ antisym. str. | 3350 m, 3336 m | 3350 m, 3339 m | 3356 s, 3339 m | 3350 m, 3342 m | 3350 m, 3342 m | 3349 m, 3334 m | 3338 s | 3335 m, 3335 m | 3332 s | 3328 m, 3276 m | 3328 m, 3276 m | 3273 m | 3273 m | |
| NH ₂ sym. str. | 3288 m, 3276 m | 3288 m, 3279 m | 3287 m, 3279 m | 3292 m, 3279 m | 3292 m, 3279 m | 3288 m, 3280 m | 3288 m, 3276 m | 3280 m | 3280 m | 2971 w | 2971 w | 2968 w | 2968 w | |
| CH ₂ antisym. str. | 2971 w | 2974 w | no | 2972 w | 2972 w | 2983 w | no | no | no | 2958 w, sh | 2958 w, sh | no | no | |
| CH ₂ antisym. str. | 2947 m, sh | no | 2940 m, sh | 2947 m, sh | 2947 m, sh | 2960 m | no | 2959 w, sh | 2959 w, sh | 2933 m, sh | 2933 m, sh | no | no | |
| CH ₂ antisym. str. | 2932 m, sh | 2934 m, sh | no | 2938 w, sh | 2938 w, sh | 2937 w, sh | 2939 w, sh | 2932 w, sh | 2932 w, sh | 2923 vs | 2923 vs | 2923 ms | 2923 ms | |
| CH ₂ sym. str. | 2920 vs | 2926 vs | 2923 vs | 2919 vs | 2919 vs | 2926 vs | 2921 vs | 2933 vs | 2921 vs | 2907 m, sh | 2907 m, sh | 2905 m, sh | 2905 m, sh | |
| CH ₂ sym. str. | 2904 m, sh | 2904 m, sh | 2903 m, sh | 2903 m, sh | 2903 m, sh | 2909 m, sh | 2901 m, sh | no | no | no | no | no | no | |
| CH ₂ sym. str. | 2889 w, sh | 2892 w, sh | no | no | no | no | no | no | no | no | no | no | no | |
| CH str. | 2850 vs | 2853 vs | 2854 vs | 2850 vs | 2850 vs | 2855 vs | 2851 vs | 2851 vs | 2851 vs | 2852 vs | 2852 vs | 2850 vs | 2850 vs | |
| NH ₂ scissoring | 1580 s | 1578 s | 1578 s | 1579 s | 1579 s | 1576 s | 1578 s | 1577 s | 1577 s | 1578 vs | 1578 vs | 1577 | 1577 | |
| | 1559 w, sh | 1560 w, sh | 1560 w, sh | 1560 w, sh | 1560 w, sh | 1559 w, sh | 1559 w, sh | 1559 w, sh | 1559 w, sh | 1561 w, sh | 1561 w, sh | 1559 | 1559 | |
| CH ₂ deform. | 1466 w, sh | 1467 w, sh | 1465 w, sh | 1466 w, sh | 1466 w, sh | 1464 w, sh | 1465 w, sh | 1463 w, sh | 1463 w, sh | 1449 s, sh | 1449 s, sh | 1449 ms | 1449 ms | |
| CH ₂ deform. | 1451 vs | 1451 vs | 1451 vs | 1452 vs | 1452 vs | 1451 vs | 1450 vs | 1456 vs | 1450 vs | 1437 w, sh | 1437 w, sh | 1437 w, sh | 1437 w, sh | |
| CH ₂ deform. | no | 1443 w, sh | 1440 w, sh | 1440 w, sh | 1440 w, sh | 1438 w, sh | no | no | no | 1384 w, sh | 1384 w, sh | 1390 w, sh | 1390 w, sh | |
| CH bending | 1386 w | 1387 w | 1389 w | 1387 w | 1387 w | 1388 w | 1384 w | 1386 w | 1384 w | 1311 w | 1311 w | 1312 | 1312 | |
| NH ₂ wagging | 1310 w | 1310 w | 1311 w | 1310 w | 1310 w | 1312 w | 1310 w | 1311 w | 1310 w | 1300 vw, sh | 1300 vw, sh | 1301 vw, sh | 1301 vw, sh | |
| NH ₂ wagging | 1305 w | 1304 vw | 1304 vw | 1303 w | 1303 w | 1307 w | 1307 w | 1307 w | 1307 w | no | no | no | no | |
| CH ₂ wagging | 1277 vw | 1276 vw | 1276 vw | 1273 vw | 1273 vw | 1276 w | 1275 w | 1274 w | 1274 w | 1255 w | 1255 w | 1256 w | 1256 w | |
| CH ₂ wagging | 1256 w | 1256 vw | 1257 vw | 1252 w | 1252 w | 1257 w | 1259 w | 1253 w | 1259 w | 1169 w | 1169 w | 1177 w | 1177 w | |
| Ring-deform. | 1170 m | 1169 m | 1169 m | 1169 m | 1169 m | 1170 m | 1172 m | 1171 m | 1172 m | 1162 w, sh | 1162 w, sh | no | no | |
| Ring deform. | 1156 w | 1157 w | 1157 w | 1158 w | 1158 w | 1160 w | 1154 w | 1158 w | 1154 w | 1114 m | 1114 m | 1114 m | 1114 m | |
| CH ₂ twisting | 1119 m | 1117 m | 1118 m | 1113 m | 1113 m | 1118 m | 1116 m | 1115 w, sh | 1116 m | 1213 m | 1213 m | 1213 m | 1213 m | |
| CH ₂ twisting | 1216 m | 1215 w | 1215 m | 1213 w | 1213 w | 1217 m | 1212 m | 1213 m | 1212 m | 1092 vw | 1092 vw | 1097 vw | 1097 vw | |
| CH ₂ twisting | 1099 w | 1094 w | 1094 w | 1093 w | 1093 w | 1099 w | 1090 w | 1095 vw | 1090 w | 1037 m | 1037 m | 1040 s | 1040 s | |
| CH ₂ twisting | 1068 w | 1065 w | 1067 w | 1063 w | 1063 w | 1065 w | no | 1067 vw | no | 1016 vs | 1016 vs | 1016 vs | 1016 vs | |
| C-N str | 1043 m | 1039 m | 1042 m | 1037 m | 1037 m | 1035 m | 1037 m | 1036 m | 1037 m | 967 m | 967 m | 966 s | 966 s | |
| C-N str | 1017 vs | 1000 vs | 1014 vs | 999 vs | 999 vs | 1014 vs | 1005 vs | 1014 vs | 1005 vs | 938 w | 938 w | no | no | |
| Ring breathing | 970 m | 967 m | 969 m | 969 m | 969 m | 968 m | 967 m | 967 m | 967 m | 919 m | 919 m | 918 w | 918 w | |
| Ring breathing | 942 vw | 942 vw | 935 vw | no | no | 934 w | 935 w | 938 w | 935 w | 890 m | 890 m | 892 s | 892 s | |
| NH ₂ twisting | 920 m | 920 m | 921 m | 918 m | 918 m | 920 m | 916 m | 920 m | 916 m | 875 w | 875 w | 880 w | 880 w | |
| Ring deformation | 892 m | 892 m | 892 m | 891 m | 891 m | 890 m | 891 m | 891 m | 891 m | 844 w | 844 w | 845 vw | 845 vw | |
| C-H bending | 880 w | 877 w | 877 m | 875 w | 875 w | 877 w | 875 w | 879 w | 875 w | 787 w | 787 w | no | no | |
| CH ₂ rocking | 845 w | 843 w | 844 w | 840 w | 840 w | 844 w | 847 w | 845 w | 847 w | 771 vw | 771 vw | 769 vw | 769 vw | |
| CH ₂ rocking | 786 w | 784 w | 784 m | 783 w | 783 w | no | 787 w, sh | 787 w | 787 w, sh | no | no | no | no | |
| Ring deformation | no | no | no | no | no | no | no | no | no | 570 m | 570 m | 570 m | 570 m | |
| CH ₂ rocking | no | no | no | no | no | no | no | no | no | 533 s | 533 s | 533 s | 533 s | |
| CH ₂ rocking | 570 s | 576 s | 569 m | 568 m | 568 m | 571 m | 574 m | 570 m | 574 m | 448 w, sh | 448 w, sh | 448 w, sh | 448 w, sh | |
| CH ₂ rocking | 533 s | 549 s | 532 s | 538 m | 538 m | 533 s | 539 m | 539 m | 539 m | 450 w, sh | 450 w, sh | 450 w, sh | 450 w, sh | |
| Ring C-N bending | 482 vw | 489 vw | 480 w | 489 vw | 489 vw | no | no | no | no | 448 w, sh | 448 w, sh | 448 w, sh | 448 w, sh | |
| | 446 w, sh | 455 w, sh | no | 447 w, sh | 447 w, sh | 448 w, sh | no | 450 w, sh | 448 w, sh | no | no | 445 w, sh | 445 w, sh | |

Abbr.: v = very, s = strong, m = medium, w = weak, no = not observed.

Table 3. n , the number of the guest molecules, included in the M-CHA-Ni hosts, and the duration of the inclusion (the time required to attain constant weight)

| Host | Guest | n | Duration (approx.) |
|-----------|---------------------|------|--------------------|
| Co-CHA-Ni | Benzene | 6.33 | 24 hours |
| Cd-CHA-Ni | | 3.20 | 70 minutes |
| Co-CHA-Ni | Toluene | 3.05 | 10 days |
| Cd-CHA-Ni | | 2.19 | 11 days |
| Co-CHA-Ni | <i>o</i> -Xylene | 1.48 | 8 days |
| Cd-CHA-Ni | | 1.98 | 8 days |
| Co-CHA-Ni | <i>m</i> -Xylene | 2.02 | 15 days |
| Cd-CHA-Ni | | 1.99 | 45 days |
| Co-CHA-Ni | <i>p</i> -Xylene | 1.47 | 15 days |
| Cd-CHA-Ni | | 1.01 | 20 days |
| Co-CHA-Ni | 1,2-Dichlorobenzene | 0.00 | 30 days |
| Cd-CHA-Ni | | 2.00 | 3 days |
| Co-CHA-Ni | 1,3-Dichlorobenzene | 0.00 | 16 days |
| Cd-CHA-Ni | | 2.00 | 16 days |
| Co-CHA-Ni | 1,4-Dichlorobenzene | 0.09 | 30 days |
| Cd-CHA-Ni | | 0.00 | 30 days |
| Co-CHA-Ni | 1,4-Dibromobenzene | 0.04 | 30 days |
| Cd-CHA-Ni | | 0.00 | 30 days |
| Co-CHA-Ni | Naphthalene | 0.01 | 8 months |
| Cd-CHA-Ni | | 1.98 | 8 months |

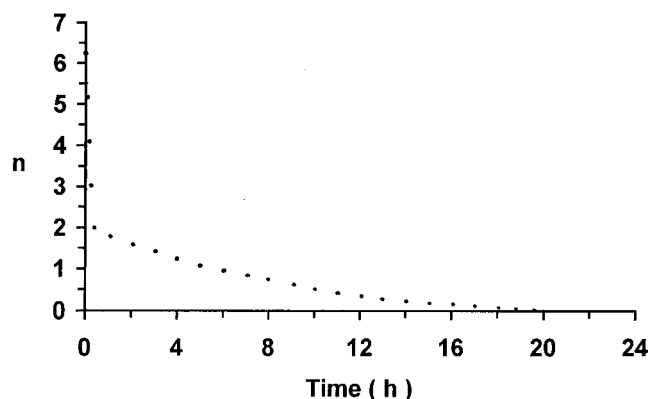


Figure 2. Decay of n (number of benzene molecules) against time for the Co-CHA-Ni-Benzene system.

partly based on the assignments of the infrared spectra of cyclobutylamine in the liquid and vapour states [12]. In order to assign the bands attributable to the CHA ligand molecules in the complex and clathrate compounds, we refer to the spectral data for the isolated (non-interacting) CHA molecule as a dilute solution (0.2 M) in an inert solvent (nujol or poly(chlorotrifluoroethylene)). The wavenumbers arising from the CHA moieties are given in Table 2a, along with the spectral data for liquid CHA and the solution of CHA in nujol and poly(chlorotrifluoroethylene) for comparison.

The N-H stretching frequencies of the CHA molecules in the complex compounds are found to be ca. 30 cm^{-1} lower than those in solution (Table 2a). These downward frequency shifts may be explained as weakening of the N-H bonds resulting from the electrons draining from the N atom on account of its coordination to the metal atom M

Table 4. The vibrational wavenumbers of benzene in the M-CHA-Ni-2Bz clathrates*

| Assignment ^a | Liquid benzene ^a | Cd-NH ₃ -Ni-2Bz ^b | Co-CHA-Ni-Bz | Cd-CHA-Ni-Bz |
|-------------------------|-----------------------------|---|---------------|--------------|
| $\nu_8 + \nu_{19}$ | 3075 | 3082 w | 3063 w | 3069 w |
| $\nu_{20} E_{1u}$ | 3073 | – | 3088 m | 3088 m |
| $\nu_{13} B_{1u}$ | 3062 | 3063 w | 3033 m | 3033 m |
| $\nu_2 A_{1g}$ | 3059 | – | no | no |
| $\nu_7 E_{2g}$ | 3046 | – | no | no |
| $\nu_5 + \nu_5 E_{14}$ | 1955 | 1986 m | 1970 w | 2967 w |
| $\nu_{10} + \nu_{17}$ | 1596 | – | no | no |
| $\nu_8 E_{2g}$ | 1815 | 1848 m | 1824 w | 1824 w |
| $\nu_{19} E_{1u}$ | 1479 | 1474 s | 1477 s | 1476 s |
| $\nu_{14} E_{2u}$ | 1309 | 1313 vw | 1303 vw | 1305 vw |
| $\nu_9 E_{2g}$ | 1178 | – | no | no |
| $\nu_{15} B_{2u}$ | 1149 | 114 s | no | no |
| $\nu_{18} E_{2u}$ | 1036 | 1032 vs | 1035 m | 1035 vw |
| $\nu_1 A_{1g}$ | 992 | – | no | no |
| $\nu_5 B_{2g}$ | 989 | – | no | no |
| $\nu_{17} E_{2u}$ | 996 | 984 m | 968 s | 966 s |
| $\nu_{10} E_{1u}$ | 849 | – | no | no |
| $\nu_{11} A_{2u}$ | 670 | 700 vs | 688 s/684/678 | 687 s |
| $\nu_6 E_{2g}$ | 606 | – | no | no |

^aTaken from Ref. [17].

^bOnly IR wavenumbers are listed without regarding assignment [8].

*Cd-NH₃-Ni-2Bz = Cd(NH₃)₂. Ni(CN)₄(2Bz), v = very, s = strong, m = medium, w = weak, no = not observed.

(Co or Cd). A metal dependent downward frequency shift is also observed for the NH₂ scissoring mode (Table 2). Similar shifts have been observed in metal-coordinated aniline compounds [13–15].

Gravimetric results and spectral changes upon enclathration

When the host complexes are subjected to the guest vapour in equilibrium with their liquid phases in a desiccator at ambient conditions, the guest molecules are sorbed by the host at a rate depending on the vapour pressure of the guest. The amount of the sorbed guest molecules was determined gravimetrically by leaving the host complex in the guest vapour to constant weight. The number of guest molecules per molecular formulae of the host complexes, n , and their sorbing duration (the times required to attain constant weight) are given in Table 3 (It should be noted that when these preparations are attempted in solution in ethanol host complexes with a much lower number of guest molecules than those in Table 3 are obtained). The most outstanding fact in Table 3 is that the number of guest benzene and toluene molecules appears to be more than the formal maximum number of 2 found in the Hofmann-type clathrates prepared previously [3]. When these clathrates are left in open air, the number of guest molecules, n , decreases rapidly down to 2, and then, continues to decrease at a slower rate. This liberation process for benzene in Co-CHA-Ni is illustrated in Figure 2, which plots the decrease of n against time. (Similar observations have been made for benzene in Cd-CHA-Ni and toluene in Co-CHA-Ni hosts.) The discontinuity at $n = 2$ on the plot suggests that the host framework with flexible ligand molecules for $n > 2$ differs from ≤ 2 . These structural changes are also indicated by the infrared spectra of the compounds

Table 5. The infrared wavenumbers of toluene in the M-CHA-Ni-2To (M=Co or Cd) clathrates and related compounds

| Assignment ^a | Toluene (Liquid) ^a | Co-daon-Ni.to ^b | Co-daon-Ni.to ^b | Co-CHA-Ni-2.to | Cd-CHA-Ni-2.to |
|---|----------------------------------|----------------------------|----------------------------|----------------|----------------|
| $\nu(\text{CH}), A_1$ | 3085 | 3080 vw | 3083 vw | 3087 w | 3087 w |
| $\nu(\text{CH}), A_1$ | 3070 | – | – | no | no |
| $\nu(\text{CH}), A_1$ | 3058 | 3061 vw | – | 3056 w | 3058 w |
| $\nu(\text{CH}), B_2$ | 3037 | 3030 w | 3030 w | 3032 vw, sh | 3032 vw, sh |
| $\nu(\text{CH}), B_2$ | 3028 | – | – | 3023 w | 3023 w |
| $\nu(\text{CH}_3), B_1$ | 2979 | 2987 m | 2980 m | 2975 w, sh | 2972 w, sh |
| $\nu(\text{CH}_3), B_2$ | 2950 | 2964 vw | 2954 vw | obsc. | obsc. |
| $\nu(\text{CH}_3), A_1$ | 2920 | – | – | obsc. | obsc. |
| $\nu(\text{CC}), A_1$ | 1604 | 1602 vw | 1600 | 1604 w | 1604 w |
| $\nu(\text{CC}), B_2$ | 1584 | 1581 s, sh | 1581 m, sh | obsc. | obsc. |
| $\nu(\text{CC}), A_1$ | 1493 | – | – | 1496 m | 1497 m |
| $\delta(\text{CH}_3), B_2$ | 1455 | 1477 m | 1477 m | obsc. | obsc. |
| $\delta(\text{CH}_3), A_1$ | 1378 | – | – | obsc. | obsc. |
| $\nu(\text{CC}), B_2$ | 1331 | – | – | no | no |
| $\beta(\text{CH}), B_2$ | 1313 | 1309 vw | 1310 vw | no | no |
| $\nu(\text{C}-\text{CH}_3)\text{X-sens}, A_1$ | 1208 | – | – | obsc. | obsc. |
| $\beta(\text{CH}), A_1$ | 1176 | 1173 vw | 1300 w | 1180 w | 1179 w |
| $\beta(\text{CH}), B_2$ | 1153 | 1155 w | 1155 w | 1159 w | 1157 w |
| $\beta(\text{CH}), B_2$ | 1080 | 1081 w | 1082 w, sh | 1080 w | 1082 w |
| $\gamma(\text{CH}_3) B_1$ | 1040 | 1043 vw | 1041 vw | 1043 m | 1040 m |
| $\beta(\text{CH}), A_1$ | 1028 | 1022 w | 1021 w | obsc. | obsc. |
| Ring, A_1 | 1002 | – | – | no | no |
| $\gamma(\text{CH}), B_1$ | 983 | – | – | no | no |
| $\gamma(\text{CH}), B_1$ | 893 | – | – | obsc. | obsc. |
| $\alpha(\text{CCC})\text{X-sens}, A_1$ | 784 | 795 w | 796 w | obsc. | obsc. |
| $\gamma(\text{CH}), B_1$ | 734 | 749 s | 750 s | 734 vs, 728 vs | 734 vs, 727 vs |
| $\phi(\text{CC}), B_2$ | 690 | 701 m | 701 m | 699 s, 694 s | 697 s, 694 s |
| | – | 687 m? | 688 m? | no | no |
| $\alpha(\text{CCC}), B_2$ | 620 | – | – | no | no |
| $\beta(\text{CCC})\text{X-sens}, A_1$ | 524 | 530 vw | 523 vw | no | obsc. |
| $\phi(\text{CCC})\text{X-sens}, B_1$ | 467 | 470 vw | – | obsc. | obsc. |

^aTaken from Ref. [18].^bTaken from Ref. [19].

Abbrs.: v = very, s = strong, m = medium, w = weak, no = not observed, obsc. = obscured by ligand.

of varying number of guest molecules. These and other notable spectral features arising from the host and the guest moieties are as follows.

As the number of guest benzene molecules gradually increases in the Co-CHA-Ni host, the band of $\text{Ni}(\text{CN})_4$ at 2153 cm^{-1} (Table 1) decreases in intensity and a corresponding new band at 2163 cm^{-1} grows in intensity. For $n = 2$, the former band (2153 cm^{-1}) disappears and the latter appears as a single band (2163 cm^{-1}). When n exceeds 2, another new band appears at 2151 cm^{-1} as a twin to the band at 2163 cm^{-1} . It is interesting to note that these twin bands of almost similar intensity are independent of the guest number for $n > 2$. These spectral features may be due to some deviation from the square planar symmetry of the $\text{Ni}(\text{CN})_4$ unit (D_{4h}) resulting in splitting of the ν_8 vibration of the degenerate E_u representation. However, this view is discounted by the evidence that the band frequencies of the twin bands ($2163/2151 \text{ cm}^{-1}$) are unchanged with respect

to the n values of 2 to 6.3 i.e., the degree of the deviation from the planar structure and, in turn, the value of the frequency splitting of the ν_8 band (E_u) should vary with the n values. In addition to this, the possibility that a Raman active mode is being observed is also discounted, since the Raman active modes (ν_1, A_{1g} and ν_4, B_{1g}) must be observed at higher frequencies than the infrared active mode ν_8, E_u [6, 10, 11]. Another conceivable suggestion may be that the primary ligand $\text{Ni}(\text{CN})_4$ behaves as a bidentate ligand (as $\text{NC-Ni}(\text{CN})_2\text{-CN}$) in the host framework. Such a $\text{NC-Ni}(\text{CN})_2\text{-CN}$ unit has also been found in some clathrates of chemical formula given for Hofmann-type clathrates [16]. It should be noted that these suggestions are tentative and possibly speculative but they are consistent with the present spectral data. Similar twin bands in $\text{Cd}(\text{CHA})_2\text{Ni}(\text{CN})_4$ for n values of 0.5 to 3.3 have been observed. Similar observations have been made for the other guest molecules (Table 1).

Table 6. The infrared wavenumbers of *o*-xylene in the clathrates

| Assignment ^a | <i>o</i> -xylene ^a (Liquid) | Co-CHA-Ni-1.5G G = <i>o</i> -xylene | Cd-CHA-Ni-2G G = <i>o</i> -xylene |
|--|---|--|--------------------------------------|
| 1, $\nu(\text{CH})$, A ₁ | 3080 | no | no |
| 21, $\nu(\text{CH})$, B ₂ | 3080 | no | no |
| 2, $\nu(\text{CH})$, A ₁ | 3064 | 3064 w | 3067 w |
| 22, $\nu(\text{CH})$, B ₂ | 3048 | 3045 w | 3047 w |
| 3, $\nu(\text{CC})$, A ₁ | 1608 | 1606 w | 1605 w |
| 23, $\nu(\text{CC})$, B ₂ no | no | no | |
| 4, $\nu(\text{CC})$, A ₁ | 1494 | 1490 w | 1491 w |
| 24, $\nu(\text{CC})$, B ₂ | 1468 | 1466 m | 1467 m |
| 5, Kekule, A ₁ | 1292 | 1285 w | 1285 w |
| 25, $\beta(\text{CH})$, B ₂ | 1290 | 1291 w | 1290 w |
| 6, X-sence., A ₁ | 1222 | no | no |
| 26, X-sens. B ₂ | 1185 | 1188 vw | 1186 vw |
| 7, $\beta(\text{CH})$, A ₁ | 1155 | obsc. | obsc. |
| 27, $\beta(\text{CH})$, B ₂ | 1121 | 1119 m | 1117 m |
| 8, $\beta(\text{CH})$, A ₁ | 1052 | 1052 m, sh | 1052 w, sh |
| 17, $\gamma(\text{CH})$, B ₁ | 930 | no | no |
| 12, $\gamma(\text{CH})$, A ₂ | (970) | no | no |
| 13, $\gamma(\text{CH})$, A ₂ | 860 | no | no |
| 28, X-sens., B ₂ | 826 | no | no |
| 18, $\gamma(\text{CH})$, B ₁ | 741 | 743 vs., 755 vs | 741 vs., 752 vs |
| 9, X-sens., A ₁ | 733 | no | no |
| 14, $\phi(\text{CC})$, A ₂ | [702] | no | no |
| 10, X-sens., A ₁ | (581) | no | no |
| 15, $\phi(\text{CC})$, A ₂ | 505 | no | no |
| 29, X-sens., B ₂ | 505 | no | 506 |
| 19, $\phi(\text{CC})$, B ₁ | 435 | 435 m, sh | 436 m, sh |
| 30, X-sens., B ₂ | 406 | nm | |
| nm 20, X-sens., B ₁ | 325 | nm | nm |
| 11, X-sens., A ₁ | 255 | nm | nm |
| 16, X-sens. A ₂ | 180 | nm | nm |
| $\nu_{\text{as}}(\text{CH}_3)$, | 2968, 2950 | 2971 w, 2947 w | 2961 w |
| $\nu_{\text{s}}(\text{CH}_3)$, | 2933 | 2933 w | 2934 w |
| $2\nu_{\text{as}}(\text{CH}_3)$, | 2882 | no | no |
| $2\delta_{\text{s}}(\text{CH}_3)$, | 2732 | 2733 w | 2732 w |
| $2\delta_{\text{as}}(\text{CH}_3)$, | 1454, 1445, 1384 | no | no |
| $\delta_{\text{s}}(\text{CH}_3)$, | 1374 | 1386 m | 1387 |
| CH ₃ rock | 1020, 984, 940 | obsc. | obsc. |

^aTaken from Ref. [20], () = infrared frequency, [] = Raman.

Abbrs.: v = very, s = strong, m = medium, w = weak, no = not observed, obsc. = obscured by ligand.

Regarding the other guests, apart from benzene and toluene, the maximum value for *n* is 2 (Table 3).

As for the spectral changes in the guest molecules, the most outstanding features are as follows: the CH out-of-plane vibrational bands are found to be shifted to higher frequencies from that of the free molecule (Tables 4–11). Similar positive frequency shifts were observed for Hofmann-type clathrates and explained as being due to the presence of a weak hydrogen bond between π electrons located above and below the plane of the benzene ring and the ammonia molecules of the host lattice [6, 7]. Similar shifts have also been found for other members of Hofmann-type

clathrates [9, 10, 14]. Therefore, we may reasonably suggest that the frequency shifts in our compounds are due to the π electron donation from the guests to the hydrogen atoms of the NH₂ group of the ligand molecule which has a more electrophilic character caused by the coordination. The values of these shifts are decreasing in the increasing order of the guest size.

Another notable feature of the CH out-of-plane vibration in benzene is that it appears as a triplet for M(en)M'(CN)₄·2C₆H₆ (M=Mn or Cd, M'=Cd or Hg) [27], a doublet for our compounds and for Cd(pyrazine)M(CN)₄·C₆H₆ (M=Cd or Hg) [28],

Table 7. The infrared wavenumbers of *m*-xylene in M-CHA-Ni-2*m*-xylene clathrates

| Assignment ^a | <i>m</i> -Xylene ^a (Liquid) | Co-dabn-Ni-G ^b G = <i>m</i> -Xylene | Cd-dabn-Ni-2G ^b G = <i>m</i> -Xylene | Cd-CHA-Ni-2G G = <i>m</i> -Xylene |
|---------------------------|---|---|--|--------------------------------------|
| $\nu(\text{CH}), B_2$ | 3052 | – | – | – |
| $\nu(\text{CH}), A_1$ | 3032 | 3024 vw | 3029 m | 3030 w |
| $\nu(\text{CC}), B_2$ | 1613 | 1623 w | 1615 m | 1615 w |
| $\nu(\text{CC}), A_1$ | 1595 | 1606 w | 1608 w, sh | 1592 w, sh |
| $\nu(\text{CC}), B_2$ | 1492 | 1487 w | 1487 w | 1489 w |
| $\nu(\text{CC}), A_1$ | 1460 | 1459 w | obsc. | obsc. |
| $\beta(\text{CH}), B_2$ | 1303 | 1308 vw | 1378 m | 1376 m |
| $\alpha(\text{CCC}), B_2$ | 1264 | 1287 vw | obsc. | obsc. |
| X-sens., A_1 | 1252 | – | obsc. | obsc. |
| $\beta(\text{CH}), B_2$ | 1167 | 1160 vw | obsc. | obsc. |
| X-sens., B_2 | 1154 | 1137 | no | 1158 vw |
| $\beta(\text{CH}), A_1$ | 1094 | 1093 vw | 1097 w | 1093 m |
| $\gamma(\text{CH}), B_1$ | 968 | – | no | no |
| X-sens., B_2 | 905 | 906 vw | 906 vw | 906 vw |
| $\gamma(\text{CH}), B_1$ | 876 | – | obsc. | obsc. |
| $\gamma(\text{CH}), B_1$ | 768 | 769 w | 769 vs | 767 vs |
| X-sens., A_1 | 7224 | – | obsc. | obsc. |
| $\pi(\text{CC}), B_1$ | 690 | 696 w | 691 s | 691 s |
| X-sens., A_1 | 537 | – | no | no |
| X-sens., B_2 | 515 | 517 w | obsc. | obsc. |
| $\pi(\text{CC}), B_1$ | 433 | – | obsc. | obsc. |
| X-sens., B_2 | 404 | – | obsc. | obsc. |

^aTaken from Ref. [21].^bTaken from Ref. [22].

Abbrs.: v = very, s = strong, m = medium, w = weak, no = not observed, obsc. = obscured by ligand.

Table 8. The infrared wavenumbers of *p*-xylene in the clathrates

| Assignment ^a | <i>p</i> -Xylene ^a (Liquid) | Co-daoc-Ni ^b <i>p</i> -Xylene | Co-CHA-Ni-1.5G G= <i>p</i> -Xylene | Cd-CHA-Ni-G G= <i>p</i> -Xylene |
|-------------------------------|---|---|---------------------------------------|------------------------------------|
| $\nu(\text{CH}), B_{1u}$ | 3044 | – | 3051 w | 3049 w |
| $\nu(\text{CH}), B_{2u}$ | 3017 | 3018 vw | 3020 w | 3020 w |
| $\nu(\text{CH}_3), B_{2u}$ | 2975, 2947 | 2985 w | obsc. | obsc. |
| $\nu(\text{CH}_3), B_{3u}$ | 2923 | – | obsc. | obsc. |
| $\nu(\text{CC}), B_{1u}$ | 1529 | 1516 w | 1517 s | 1516 s |
| $\delta(\text{CH}_3), B_{3u}$ | 1458, 1452 | 1475, sh | obsc. | obsc. |
| $\nu(\text{CC}), B_{3u}$ | 1421 | 1435 vw | no | no |
| $\delta(\text{CH}_3), B_{2u}$ | 1379 | – | obsc. | obsc. |
| $\alpha(\text{CCC}), B_{2u}$ | 1324 | – | no | no |
| X-sens., B_{2u} | 1220 | – | no | no |
| $\beta(\text{CH}), B_{2u}$ | 1120 | 1119 vw | 1118 m | 1116 w |
| $\gamma(\text{CH}_3), B_{2u}$ | 1041 | 1049 m | 1040 w, sh | no |
| $\beta(\text{CH}), B_{1u}$ | 1023 | 1022 vw | obsc. | obsc. |
| $\gamma(\text{CH}), B_{3u}$ | 795 | 796 s | 796 vs | 795 vs |
| X-sens., B_{1u} | 725 | 729 m | obsc. | obsc. |
| $\phi(\text{CC}), B_{3u}$ | 483 | 484 w | obsc. | obsc. |

^aTaken from Ref. [23].^bTaken from Ref. [19].

Abbrs.: v = very, s = strong, m = medium, w = weak, no = not observed, obsc. = obscured by ligand.

Table 9. The infrared wavenumbers of 1,2-dichlorobenzene in the M-CHA-Ni-2 1,2 dichlorobenzene clathrates and related compounds

| Assignment ^a | 1,2-dichlorobenzene ^a in CCl ₄ or CS ₂ | Co-daon-Ni-2G ^b G = 1,2-dichlorobenzene | Cd-daon-Ni-2G ^b G = 1,2-dichlorobenzene | Cd-CHA-Ni-2G G = 1,2-dichlorobenzene |
|-------------------------------------|--|---|---|---|
| 1, ν(CH) A ₁ | 3072 | 3078 vw | 3082 w | 3072 w |
| 21, ν(CH) B ₂ | 3072 | | | |
| 2, ν(CH) A ₁ | no | | | |
| 22, ν(CH) B ₂ | no | | | |
| 3, ν(CC) A ₁ | 1576 | 1571 m | 1570 m | obsc. |
| 23, ν(CH) B ₂ | 1576 | | | |
| 4, ν(CH) A ₁ | 1458 | 1455 s | 1454 s 143 m, sh | |
| 24, ν(CH) B ₂ | 1438 | 1434 m | 1434 m | 1436 m |
| 5, Kekule A ₁ | 1276 | | | |
| 25, ν(CH) B ₂ | 1252 | 1249 w | 1259 w | no |
| 6, X-sens., A ₁ | 1155 | 1157 m | 1157vw | obsc. |
| 26, X-sens., B ₂ | 1130 | 1122 m | 1123 m | 1125 s |
| 7, β(CH) A ₁ | 1130 | | | 1125 s |
| 27, β(CH) B ₂ | 1038 | 1037 s | 1035 s | 1036 vs |
| 8, β(CH) A ₁ | no | | | |
| 12, γ(CH) A ₂ | 975 | – | – | obsc. |
| 17, γ(CH) B ₁ | 940 | 947 vw | 947 | 949 w |
| 13, γ(CH) A ₂ | 850 | 859 vw | 843 vw | obsc. |
| 18, γ(CH) B ₁ | 748 | 760 vs | 760 vs | 748 vs |
| 28, X-sens., B ₂ | 740 | 736 vs | 736 vs | 762 vs |
| 14, φ(CC) A ₂ | no | | | |
| 9, X-sens., A ₁ | 660 | 660 s | 659 s | 659 s |
| 10, X-sens., A ₁ | 480 | 486 vw | 481 vw | obsc. |
| 15, φ(CC) A ₂ | no | | | no |
| 19, φ(CC) B ₁ | 435 | – | – | no |
| 29, X-sens., B ₂ | 427 | – | – | no |
| 30, X-sens., B ₂ | 336 | | | |
| 20, X-sens., B ₁ | 239 | | | nm |
| 11, X-sens., A ₁ | 202 | | | nm |
| 16, X-sens., A ₂ | 152 | | | nm |
| ν _s (CH ₃) | 2977, 2950 | | | |
| ν _s (CH ₃) | 2922 | | | no |
| | 2856 | | | no |
| 2δ _{as} (CH ₃) | 2742 | | | no |
| 2δ _s (CH ₃) | 1458, 1439 | | | 1456 s |
| δ _{as} (CH ₃) | 1382 | | | 1382 w |
| δ _s (CH ₃) | no | | | no |
| (CH ₃) rock | 1042, 988 | | | no |

^aTaken from Ref. [20].

^bTaken from Ref. [24].

Abbrs.: v = very, s = strong, m = medium, w = weak, no = not observed, obsc. = obscured by ligand, nm = not measured.

M(NH₃)₂M'(CN)₄·2C₆H₆ (M=Mn or Cd, M'=Cd or Hg) [29] and M(tn)Zn(CN)₄·2C₆H₆ (M=Mn or Zn) [30], a singlet for M(NH₃)₂Ni(CN)₄·2C₆H₆ (M=Mn, Fe, Ni, Cu, Zn or Cd) [6, 8] and Cd(4,4'-bipyridyl) M'(CN)₄·2C₆H₆ (M'=Cd or Hg) [31]. In the case of doublet or triplet features the splittings have been ascribed to crystal field effects (strong host-guest interactions) [6–8, 27–31]. In the case of a single band, because of the larger cavities due to the ligands, the host-guest interactions are expected not to be effective for splitting [31]. Splitting has also been observed for toluene (Table 5) and *o*-xylene (Table 6). The band positions of

benzene and toluene do not depend on the value of *n* (*n* ≤ 2 or *n* > 2); the only differences are in the band intensities.

The noteworthy spectral features arising from the ligand molecules on guest inclusion are as follows: on going from the host complex to the clathrate the symmetric and asymmetric stretching frequencies of NH₂ decrease (Table 2a, b). This downward shift may be due to hydrogen bonding between the π electron of the guest ring(s) and the cyclohexylamine ligand molecules, as has been suggested for the Hofman-type benzene clathrates with amine and diamine ligands [27, 30].

Table 10. The infrared wavenumbers of 1,3-dichlorobenzene in the Cd-CHA-Ni1,3 dichlorobenzene clathrate and related compounds

| Assignment ^a | | 1,3-dichlorobenzene ^a (liquid) | 1,3-dichlorobenzene ^b (in CCl ₄ or CS ₂) | Cd-CHA-Ni-2G G = 1,3-dichlorobenzene |
|---------------------------------------|--------------------------------------|--|---|---|
| A ₁ ν ₁ ν(CH), | 3071 | 3071 | 3069 w | |
| | ν ₂ ν(CH), | | | no |
| | ν ₃ ν(CH), | | | no |
| | ν ₄ ν(CC), | 1577 | 1580 | 1578 vs |
| | ν ₅ ν(CC), | 1412 | 1412 | 1413 |
| | ν ₆ X-sens., | 1124 | 1127 | 1124 m |
| | ν ₇ ν ₇ ν(CH), | 1073 | | 1072 m |
| | ν ₈ ring, | 997 | 1000 | 999 s |
| | ν ₉ X-sense. | 663 | 663 | 663 |
| | ν ₁₀ X-sense. | 398 | 399 | no |
| | ν ₁₁ X-sens., | 198 | 198 | no |
| A ₂ | ν ₁₂ γ(CH), | 892 | 896 | 890 m |
| | ν ₁₃ ν(CC) | 532 | | 529 |
| | ν ₁₄ X-sens., | | | |
| B ₁ | ν ₁₅ γ(CH), | 964 | 966 | 967 m |
| | ν ₁₆ γ(CH) | 867 | 869 | 867 m |
| | ν ₁₇ γ(CH) | 773 | 775 | 774 s |
| | ν ₁₈ φ(CC) | 672 | 674 | 674 s |
| | ν ₁₉ ν(CC) | 433 | 428 | no |
| | ν ₂₀ X-sens., | 175 | | nm |
| B ₂ ν ₂₁ ν(CH), | 3095 | 3095 | 3092 w | |
| | ν ₂₂ ν(CC) | 1577 | 1580 | 1580 vs |
| | ν ₂₃ ν(CC=), | 1462 | 1464 | 1462 vs |
| | ν ₂₄ β(CH), | 1289 | 1330 | 1341 w, sh |
| | ν ₂₅ Kekule | 1258 | 1258 | 1255 w |
| | ν ₂₆ ν(CH), | 1161 | 1161 | 1162 w |
| | ν ₂₇ X-sens., | 1080 | 1079 | 1081 m |
| | ν ₂₈ X-sens., | 784 | 784 | 783 vs |
| | ν ₂₉ X-sens., | | | |
| | ν ₃₀ X-sens., | 365 | 364 | nm |

^aTaken from Ref. [21].

^bTaken from Ref. [25].

Abbrs.: v = very, s = strong, m = medium, w = weak, no = not observed, nm = not measured.

Based on the present data, it is not possible to determine the configuration of the ligand or guest molecules in the clathrate studies. As in the Hofmann-type and Hofmann-T_d-type benzene clathrates, the relative orientation of the N–H bonds of cyclohexylamine with respect to the axis of the π cloud of the guest must be the one most favourable for hydrogen bonding [32].

Selective absorption and separation of guest molecules

The phenomena just described implies the employability of the host complexes for selective absorption and separations of isomeric guest molecules. For these purposes three experiments have been performed: (i) When the host complex Cd-CHA-Ni was placed in a desiccator containing a mixture of benzene and toluene vapour with a mole ratio of 1/1, the benzene clathrate was obtained after a week. Infrared spectra

of this show no sign of a toluene molecule in the compound, only benzene ($n = 5.8$). In the case of the Co-CHA-Ni complex, however, both benzene and toluene are sorbed. (ii) When the toluene clathrate Cd-CHA-Ni-to was placed in a desiccator containing benzene and toluene vapour as before, the benzene clathrate was obtained after two weeks ($n = 5.9$). (iii) The host complexes absorb both *m*-xylene and *p*-xylene, but not *o*-xylene, from the *o*-, *m*- and *p*-xylene mixture with mole ratios of 1 : 1 : 1. These promising results suggest that the host complex compounds presented here may be employed for selective absorption and separation of isomers.

It should be noted that experiments with a large number of aromatic guest molecules and host complexes with M=Mn, Fe, Cu, Ni, Zn or Cd, M'=Ni, Pd or Pt and a series of cycloalkylamines (cyclopropylamine, cyclobutylamine, cyclopentylamine, cyclohexylamine, cycloheptylamine, cyc-

Table 11. The infrared wavenumbers of naphthalene in Cd-CHA-Ni-Npth. clathrates

| Assignment ^a | Naphthalene ^a (in CCl ₄ or CS ₂) | Cd-daon-Ni-G ^b G = Naphthalene | Cd-CHA-Ni-2G G = Naphthalene |
|---------------------------------------|---|--|---------------------------------|
| 41 CH str., B _{3u} | 3072 vs | 3062 w | 3065 w |
| 29 CH str., B _{2u} | 3014 s | 3012 vw | 3012 vw, sh |
| 42 CH str., B _{3u} | 2976 s | 2979 m | no |
| 30 CH str., B _{2u} | 2947 m | 2960 vw | no |
| 43 CC str., B _{3u} | 1680 m | – | no |
| 31 CC str., B _{2u} | 1595 s | 1593 s, sh | 1596 m, sh |
| 44 CC str., B _{3u} | 1510 m | 1504 m | 1507 m |
| 32 CC str., B _{2u} | 1387 vs | 1387 w | 1390 m |
| 33 CH bend, B _{2u} | 1268 vs | 1269 m | 1269 s |
| 45 CH bend, B _{3u} | 1211 s | – | 1213 m |
| 34 CH bend, B _{2u} | 1139 s | 1130 w | 1130 m |
| 46 CH bend, B _{3u} | 1012 s | 1011 w | 1010 m, sh |
| 22 CH bend, B _{1u} | 957 s | – | no |
| 47 skeletal breat, B _{3u} | 876 m | – | 880 |
| 23 CH bend, B _{1u} | 782 vs | 796 vs | 786 vvs |
| 35 skeletat distort., B _{2u} | 752 s | 754 vw | 754 vw |
| 48 skeletat distort., B _{3u} | 618 s | 619 w | 618 m |
| 24 CC distort., B _{1u} | 475 s | 480 s | 480 m |

^aTaken from Ref. [26].

Abbrs.: v = very, s = strong, m = medium, w = weak, no = not observed.

looctylamine, cyclododecylamine, cyclohexyldiamine, cycloheptyl cyanide, cycloheptanecarbonitrile, cyclohexanecarbonitrile, cyclohexyl isocyanide, cyclohexyl isothiocyanate and cyclohexyl mercaptan) are in progress.

References

- R.F. Evans, O. Ormrod, B.B. Goalby, and L.A.K. Stavely: *J. Chem. Soc.* 3346 (1950).
- U.S. Patent, 2, 732, 413 (1956).
- T. Iwamoto: *The Hofmann-type and Related Inclusion compounds* (Inclusion compounds, Vol. 4, J.L. Atwood, J.E.D. Davies and D.D. MacNicol (eds.), pp. 29–57, Academic Press (1984).
- S. Nishikiori and T. Iwamoto: *Chem. Lett.* 1035 (1982).
- Y. Mathey and C. Mazieres: *Can. J. Chem.* **52**, 3637 (1974).
- S. Akyüz, A.B. Dempster, R.L. Morehouse, and S. Susuki: *J. Mol. Struct.* **17**, 105 (1973).
- S. Akyüz, A.B. Dempster, and R.L. Morehouse: *Spectrochim. Acta* **30A**, 1183 (1974).
- S. Akyüz, A.B. Dempster, and R.L. Morehouse: *Spectrochim. Acta* **30A**, 1189 (1974).
- S. Bayarı, Z. Kantarcı, and S. Akyüz: *J. Mol. Struct.* **351**, 19 (1995).
- N. Karacan, Z. Kantarcı, and S. Akyüz: *Spectrochim. Acta* **A52**, 771 (1996).
- R.L. McCullough, L.H. Jones, and G.A. Croaby: *Spectrochim. Acta* **16**, 929 (1960).
- A.O. Diallo, N.V. Thanh, and I. Rossi: *Spectrochim. Acta* **43A**, 415 (1987).
- S. Akyüz and J.E.D. Davies: *J. Mol. Struct.* **97**, 457 (1982).
- S. Bayar, C. Bayrak, and Z. Kantarcı: *J. Incl. Phenom.* **38**, 23 (2000).
- D.A. Thornton: *J. Coord. Chem.* **24**, 261 (1991).
- T. Iwamoto, *J. Incl. Phenom.* **24**, 61 (1996).
- P.C. Painter and J.L. Koenig: *Spectrochim. Acta.* **33A**, 1003 (1977).
- A.P. Hitchcock and J.D. Laposa: *J. Mol. Spectrosc.* **54**, 223 (1975).
- E. Kasap and A. Özbay: *J. Incl. Phenom.* **28**, 335 (1997).
- J.H.S. Green: *Spectrochim. Acta.* **26A**, 1913 (1970).
- J.H.S. Green: *Spectrochim. Acta.* **26A**, 1523 (1970).
- S. Sağlam, T.R. Sertbakan, E. Kasap, and Z. Kantarcı: *J. Mol. Struct.* **482–483**, 69 (1999).
- J.H.S. Green: *Spectrochim. Acta.* **26A**, 1503 (1970).
- T.R. Sertbakan, E. Kasap, and Z. Kantarcı: *J. Mol. Struct.* **482–483**, 75 (1999).
- J.R. Schever and J.C. Evans: *Spectrochim. Acta* **19**, 1739 (1963).
- E.R. Lippincott and E.J. O'Reilly: *J. Chem. Phys.* **23**, 238 (1955).
- E. Kasap and Z. Kantarcı: *J. Incl. Phenom.* **23**, 1 (1995).
- N. Ekici, Z. Kantarcı, and S. Akyüz: *J. Incl. Phenom.* **10**, 9 (1991).
- E. Kasap and Z. Kantarcı: *J. Incl. Phenom.* **20**, 33 (1995).
- Z. Kantarcı and C. Bayrak: *J. Incl. Phenom.* **30**, 59 (1998).
- S. Bayarı, Z. Kantarcı, and S. Akyüz: *J. Incl. Phenom.* **17**, 291 (1998).
- E. Ruiz, J.J. Novoa, and S. Alvarez: *J. Phys. Chem.* **99**, 2296 (1995).