

## Infrared Spectroscopic and Gravimetric Studies on the Dicyclopentylaminemetal(II) Tetracyanonickellate(II) Host–Aromatic Guest Systems

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### Abstract

The host complexes  $M(\text{Cyclopentylamine})_2\text{Ni}(\text{CN})_4$  ( $M=\text{Co}$  or  $\text{Cd}$ ) have been prepared in powder form. The spectral data suggest that the structures of these compounds are similar to those of the Hofmann-dma-type hosts. The absorption and the liberation processes of the aromatic guests (benzene, toluene, 1,2-, 1,3-, 1,4-dichlorobenzene, 1,4-dibromobenzene *o*-, *m*-, *p*-xylene, naphthalene) 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 do not change on inclusion and liberation of the guests. The host compounds have been suggested as sorbents for isomeric separations.

### Introduction

Hofmann-type host complexes are formulated as  $\text{ML}_2\text{M}'(\text{CN})_4$  ( $M = \text{Mn, Fe, Co, Ni, Cu, Zn}$  or  $\text{Cd}$ ;  $\text{M}' = \text{Ni, Pd}$  or  $\text{Pt}$ ;  $\text{L} = \text{unidentate ligand}$ ) (Figure 1). The framework of these hosts consists of two-dimensional polymeric layers formed from  $\text{ML}_2$  cations and  $\text{M}'(\text{CN})_4$  anions. The  $\text{M}'$  atom is bonded to four C atoms of the CN groups in a square-planar geometry. The  $\text{M}$  atom is octahedrally surrounded by six N atoms, four from the CN units and the other two are from two ligand molecules. The ligand molecules lie above and below the layers. The ligand and the layers as blocking units provide empty voids of varying shapes and dimensions, in which guest molecules may be imprisoned [1].

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 clathrate and host compounds [1–3]. Of these, dimethylamine (dma) [1] and cyclohexylamine (CHA) [3] give a number of inclusion compounds with a selectivity very different from the Hofmann-type hosts. The hosts  $\text{Cd}(\text{dma})_2\text{Ni}(\text{CN})_4$  [1] and  $\text{M}(\text{CHA})_2\text{Ni}(\text{CN})_4$  ( $M = \text{Co}$  or  $\text{Cd}$ ) [3] can include, besides benzene, a number of large aromatic guests (some benzene derivatives and naphthalene) which have never been found enclathrated into Hofmann-type and the analogous hosts. Some of the inclusion compounds with dma show X-ray diffraction patterns characteristic of the intercalate structures of these guests

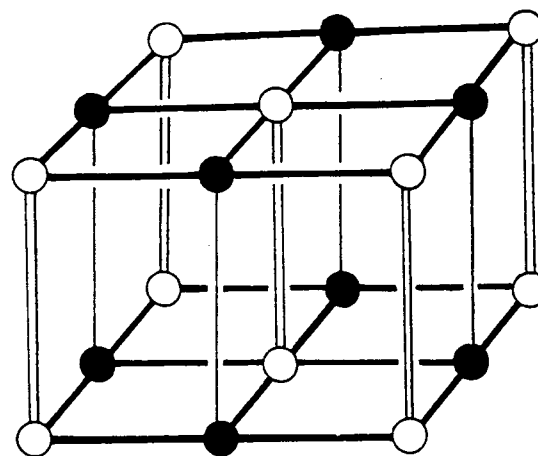


Figure 1. The model for the Hofmann-diam-type host structure (open circle: 6-coordinate M, solid circle: square-planar Ni, open column: an ambident ligand, thick line: CN bridge and thin line: edge of cavity).

between the layered metal complex sheets. The expanded spacing has been interpreted in term of the guest molecules arranged between sheets covered with hydrophobic methyl groups which may form a tunnel-like cavity between the sheets [1].

These unusual results have encouraged us to explore the inclusion behaviour of the Hofmann-type and Hofmann-T<sub>d</sub>-type clathrates, with a series of cycloalkylamines and a variety of guest molecules different in size and shape from those enclathrated in the Hofmann-type and Hofmann-T<sub>d</sub>-type hosts.

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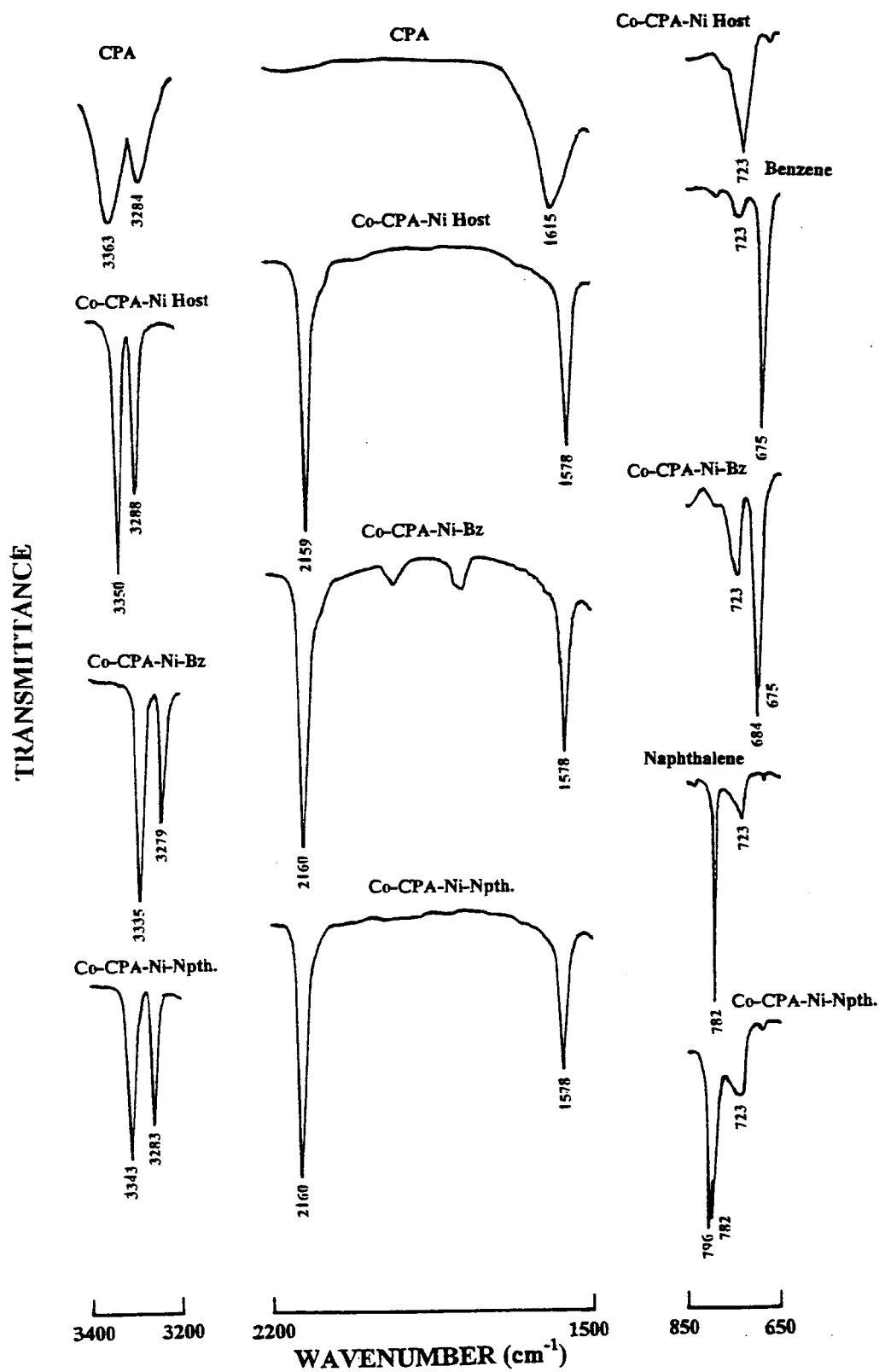


Figure 3. The important IR band of CPA, Ni(CN)<sub>4</sub>, benzene and naphthalene species in different chemical states related to the Co-CPA-Ni-Guest system (all compounds are in nujol).

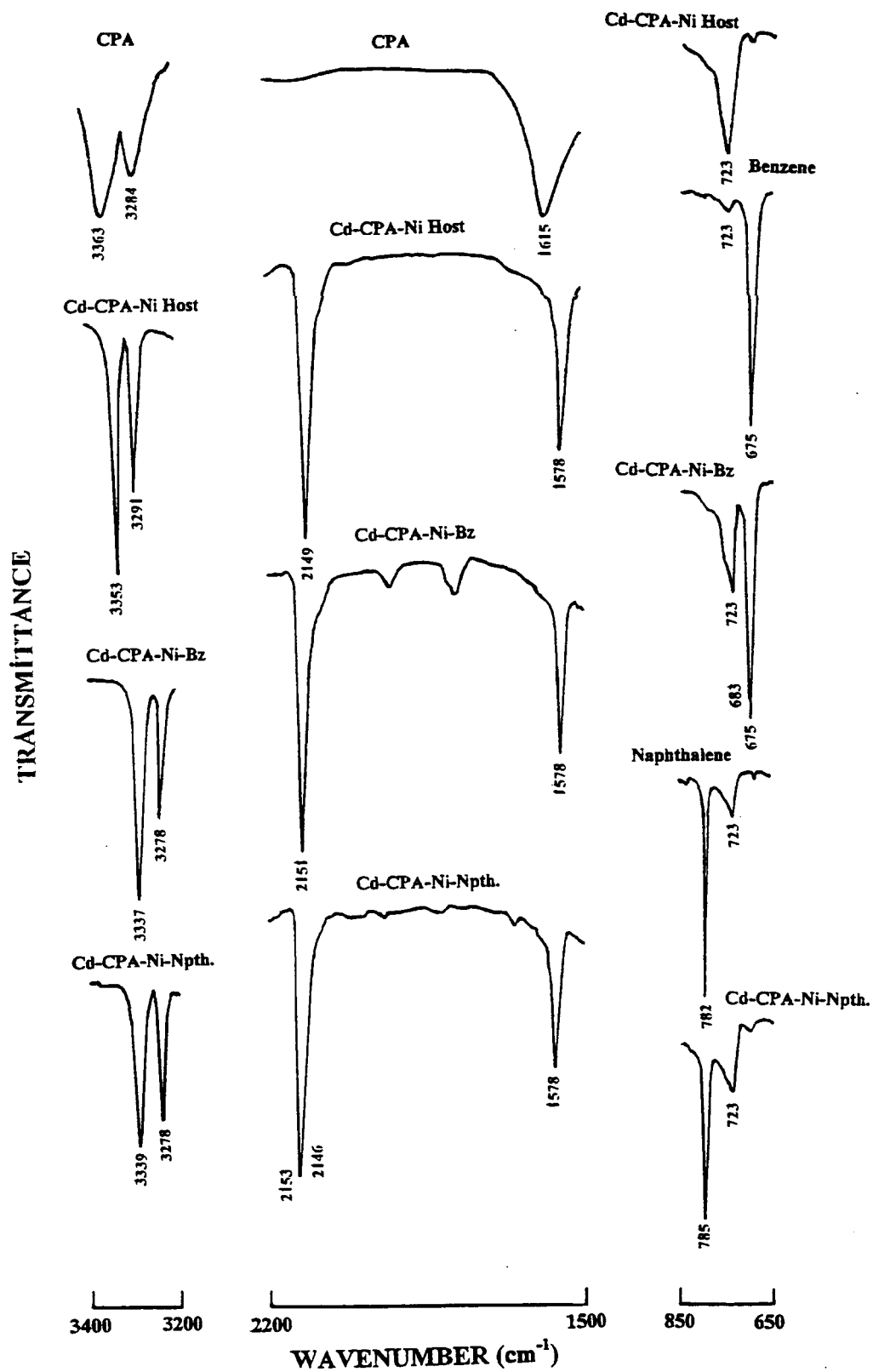


Figure 4. The important IR bands of CPA, Ni(CN)<sub>4</sub>, benzene and naphthalene species in different chemical states related to the Cd-CPA-Ni-Guest system (all compounds are in nujol).

## Results and discussion

For comparison and discussion the important spectral regions of CPA, Ni(CN)<sub>4</sub>, benzene and naphthalene species in different chemical states are shown in Figures 3 and 4.

Before dealing with the inclusion and liberation of the guest species in the host complexes, it is appropriate to elucidate the host framework on the basis of the available spectral data.

The spectral features of the host compounds under study are found to be similar to each other suggesting that they also possess similar structural features. It will be convenient to divide the vibrations into two, arising from the Ni(CN)<sub>4</sub> group and from the CPA ligand. The assignment of the spectral bands due to the Ni(CN)<sub>4</sub> species are straightforward, since these bands are persistent and picked out with ease [3, 4–9].

### *Ni(CN)<sub>4</sub> group vibrations*

The fact that in the host framework of the Hofmann-type clathrates [1–3, 6, 7] and Hofmann-type host complexes [4, 7, 8], the metal atom Ni in Ni(CN)<sub>4</sub> is square planarly surrounded by the carbon ends of the CN ions suggests that the host framework of the complexes studied also have square planar Ni(CN)<sub>4</sub> units. In order to assign the bands attributable to the Ni(CN)<sub>4</sub> ion in the spectra, we refer to the work of McCullough et al. who presented vibrational data for the salt Na<sub>2</sub>Ni(CN)<sub>4</sub> in the solid state [9]. In this salt the Ni(CN)<sub>4</sub> anion is not coordinated to Na<sup>+</sup> ion; therefore, it can be treated as an isolated unit with D<sub>4h</sub> symmetry and thus used as reference to comment on vibrational changes when Co–NC (or Cd–NC) bonding takes place. The spectral data for Ni(CN)<sub>4</sub> groups in the host complexes and clathrates are given in Table 1, together with the spectral data of Na<sub>2</sub>Ni(CN)<sub>4</sub>. The assigned wavenumber of the Ni(CN)<sub>4</sub> units of the complexes studied are much higher than those for the isolated Ni(CN)<sub>4</sub> ion (Table 1). Such frequency shifts have been observed for Hofmann-type host frameworks [4–8], and are attributed to the mechanical coupling of the internal modes of Ni(CN)<sub>4</sub> with the M–NC vibrations. It follows that the N-termini of the Ni(CN)<sub>4</sub> group are bound to a Co (or Cd) atom in the host complexes.

### *CPA (cyclopentylamine) vibrations*

The assignments and the wavenumbers of the vibrational bands of CPA observed in the infrared spectra of the compounds under study are given in Table 2, together with the spectral data for CPA in the gas phase [10] on which the assignments are based.

The N–H stretching frequencies of the CPA molecules in the host complexes are found to be ca. 50 cm<sup>-1</sup> lower than those of CPA in the gas phase (Table 2). 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 or Cd). A metal dependent downward frequency shift is also observed for the NH<sub>2</sub> scissoring mode

(Table 2). Similar shifts have been observed in the M (cyclohexylamine)<sub>2</sub>Ni(CN)<sub>4</sub> (M Co or Cd) host complexes [3].

### *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 vapor 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. *n*, the number of the guest molecules per molecular formula of the host complexes, and their sorbing duration (the time 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 benzene and toluene molecules appears to be more than the formal maximum number of 2 found in the Hofmann-type clathrates prepared previously [1]. When these clathrates are left in open air, the number of guest molecules, *n*, decreases rapidly down to ca. 2, and then continues to decrease at a slower rate. This liberation process for benzene from Co–CPA–Ni is illustrated in Figure 2, which plots the decrease of *n* against time. (Similar observations have been made for benzene from Cd–CPA–Ni and toluene in Co–CPA–Ni hosts). The curvature at *n* = 2 on the plot (Figure 2) suggests that the inclusion compounds for guest molecules for *n* ≤ 2 are more stable than for *n* > 2. Similar observations have been made for the M–CHA–Ni–G (M = Co or Cd, G = benzene or toluene systems) [3].

The notable spectral changes upon enclathration are as follows: of the host moieties with the exception of Cd–CPA–Ni in the naphthalene clathrate, the Ni(CN)<sub>4</sub> unit does not exhibit considerable spectral changes upon sorption (Table 1). These results suggest that the planar structure of [M–Ni(CN)<sub>4</sub>]<sub>∞</sub> is preserved (for all *n* values) upon enclathration. Substantial spectral changes for the Ni(CN)<sub>4</sub> unit in the dicyclohexylaminemetal(II) tetracyanonickellate(II) host-aromatic guest systems have however been observed and attributed to the substantial structural changes of the Ni(CN)<sub>4</sub> unit [3]. In the case of Cd–CPA–Ni–1.85Npth two bands (as a doublet) are observed at 2153 and 2146 cm<sup>-1</sup>. This spectral feature may be due to the fact that the primary ligand Ni(CN)<sub>4</sub> behaves as a bidentate ligand (as NC–Ni(CN)<sub>2</sub>–CN) in the host structure.

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 the NH<sub>2</sub> unit decreases. This downward shift may be due to hydrogen bonding between the π electron of the guest ring(s) and the cyclopentylamine ligand molecules, as has been suggested for the Hofmann-type benzene clathrates with amine and diamine ligands [16, 19]. Another notable feature is that the ω(NH<sub>2</sub>) and δ(NH<sub>2</sub>) vibrations appear at higher frequencies when com-

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

Assignment <sup>a,b</sup>	CPA(IR) <sup>a,b</sup> (Gas)	Co-CPA-Ni	Cl-CPA-Ni	Co-CPA-Ni-2G G = Benzene	Cl-CPA-Ni-2G G = Benzene	Co-CPA-Ni-2G G = Toluene	Cl-CPA-Ni-2G G = Toluene	Co-CPA-Ni-1.5G G = o-Xylene
$\nu_{24}$ , NH <sub>2</sub> antisym. str	3400 vw	3350 s	3353 s	3335 s	3337 s	3338 s	3337 s	3339 s
$\nu_7$ -NH <sub>2</sub> symmetric stretch	3339 w	3288 m	3291 m	3279 m	3278 m	3281 m	3281 m	3280 m
$\nu_2$ and $\nu_{25}$ , $\beta$ -CH <sub>2</sub> antisymmetric stretch	2968 vvs	2948 vs	2950 vs	2952 vs	2950 vs	2952 vs	2952 vs	2947 vs
$\nu_3$ , $\alpha$ -CH stretch	2875 vvs	2913 m, sh	2911 m, sh	2907 w, sh	2916 m, sh	2922 m, sh	2925 w, sh	2927 w, sh
$\nu_4$ , $\nu_{26}$ , $\beta$ -CH <sub>2</sub> symmetric stretch	2700 w	2863 s	2861 s	2865 s	2861 s	2870 s	2869 s	2867 s
$\nu_7$ -NH <sub>2</sub> deformation	1624 Q, s	1450 m	1451 m	1456 w	1451 w	1457 m	1457 w	1456 m
$\nu_9$ , $\nu_{30}$ , $\beta$ -CH <sub>2</sub> deformations	1356 s	1379 m	1379 m	1378 m	1378 m	1378 m	1378 m	1376 m
$\nu_{10}$ , $\alpha$ -C-H in-plane bend	1322 vvw	1306 w	1306 w	1306 vw	1306 vw	1311 vw	1308 vw	1306 vw
$\nu_{11}$ , $\gamma$ -CH <sub>2</sub> symmetric wag	1204 (sh)	1211 w	1213 w	1207 w	1210 w	1210 w	1211 w	1208 w
$\nu_{14}$ , C-N stretch	1176 w	1167 w	1171 w	1168 w	1170 w	1179 w	1169 w	1171 w
$\beta_{15}$ , $\beta$ -CH <sub>2</sub> symmetric twist	1056 Q, m	1059 m	1061 m	1066 m	1065 m	1065 m	1065 m	1065 m
$\nu_{35}$ , $\alpha$ -CH out-of-plane bend	1012 Q, w	1013 s	1006 s	1014 s	1009 s	1016 s	1004 s	1016 s
$\nu_{36}$ , $\nu_{37}$ , ring deformation	1003 sh	992 m, sh	992 m, sh	996 m, sh	993 m, sh	994 m, sh	991 m, sh	993 m, sh
$\nu_{38}$ , $\gamma$ -CH <sub>2</sub> antisymmetric rock	948 w	941 w	943 w	936 w	938 w	936 w	938 w	964 w
$\nu_{39}$ , NH <sub>2</sub> twist		920 w, sh	921 w, sh	no	919 vw	no	920 vw	920 vw
$\nu_{17}$ , ring breathing mode	803 Q, sh	827 w	828 w	892 w	894 w	894 w	893 w	893 w
$\nu_{20}$ , NH <sub>2</sub> wag	770 vw	770 w	769 w	770 w	771 vw	832 vw	826 vw	828 vw
$\nu_{41}$ , $\beta$ -CH <sub>2</sub> antisymmetric rock		568 m	556 m, sh	564 m, sh	556 m, sh	769 w, sh	767 w, sh	758 m, sh
$\nu_{21}$ , ring deformation	545 sh	551 m	536 s	532 m	535 m	564 m, sh	556 m, sh	566 m, sh
$\nu_{22}$ , C-N in-plane bend	462 Q, sh	482 vw	480 vw	481 vw	482 vw	551 m	480 vw	552 m
	455 P	448 w, sh	448 w, sh	455 m, sh	446 w, sh	481 vw	480 vw	480 vw
						456 w, sh	447 w, sh	456 w, sh

<sup>a</sup> Taken from Ref. [10]. Abbrev: v = very, s = strong, m = medium, w = weak, sh = shoulder and no = not observed.

<sup>b</sup>  $\nu_{14}$ (C-Nstr.),  $\nu_{34}$ ( $\beta$ -CH<sub>2</sub> antisym. twist),  $\nu_{35}$ ( $\alpha$ -CH out-of-plane bend) and NH<sub>2</sub> wag bands of CPA(gas) are not observed in the compounds studied.

Table 2b. Assignment and the wavenumbers for the CPA in the clathrates

Assignment <sup>a,b</sup>	CPA(IR) <sup>a,b</sup> (Gas)	Cd-CPA-Ni-2G G = <i>o</i> -Xylene	Co-CPA-Ni-2G G = <i>m</i> -Xylene	Cd-CPA-Ni-2G G = <i>m</i> -Xylene	Co-CPA-Ni-2G G = <i>p</i> -Xylene	Cd-CPA-Ni-2G G = <i>p</i> -Xylene	Co-CPA-Ni-2G G = 1,2-dichlorobenzene	Cd-CPA-Ni-2G G = 1,2-dichlorobenzene
$\nu_{24}$ , NH <sub>2</sub> antisym. str	3400 vw	3341 s	3342 s	3354 s	3329 s	3354 s	3342 s	3342 s
$\nu_7$ -NH <sub>2</sub> symmetric stretch	3339 w	3281 m	3281 m	3291 m	3283 m, sh	3290 m	3284 m	3283 m
$\nu_2$ and $\nu_{25}$ , $\beta$ -CH <sub>2</sub> antisymmetric stretch	2968 vs	2949 vs	2951 vs	2952 vs	2952 vs	2950 vs	2956 vs	2955 vs
$\nu_3$ , $\alpha$ -CH stretch		2923 m, sh	2929 m, sh	2928 m, sh	2925 m, sh	2929 m, sh	2914 m, sh	2915 m, sh
$\nu_4$ , $\nu_{26}$ , $\beta$ -CH <sub>2</sub> symmetric stretch	2875 vs	2870 s	2869 s	2867 s	2868 s	2870 s	2870 s	2870 s
$\nu_7$ -N <sub>2</sub> deformation	2700 w	2729 w	2735 w	2736 w	2734 w	2729 w	2725 w	2725 w
$\nu_9$ , $\nu_{30}$ , $\beta$ -CH <sub>2</sub> deformations	1624 Q, s	1581 s	1580 s	1578 s	1581 s	1578 s	1578 s	1578 s
$\nu_{10}$ , $\alpha$ -C-H in-plane bend	1461 Q, s	1457 m	1453 w	1452 m	1453 m	1452 m	1457 vs	1457 s
$\nu_{11}$ , $\gamma$ -CH <sub>2</sub> symmetric wag	1356 s	1378 m	1376 m	1377 m	1380 m	1379 m	1375 m	1375 m
$\nu_{14}$ , C-N stretch	1322 vw	1306 w	1305 vw	1306 vw	1306 vw	1306 vw	no	no
$\nu_{15}$ , $\beta$ -CH <sub>2</sub> symmetric twist	1204 (sh)	1208 w	1208 w	1208 w	no	1209 w	1285 w	1218 w
$\nu_{35}$ , $\alpha$ -CH out-of-plane bend	1176 w	1171 w	1171 w	1170 w	1177 w	1170 w	1167 w	1170 w
$\nu_{36}$ , $\nu_{37}$ , ring deformation	1148 m	1148 m	1157 m	1149 m	1155 m	1152 m	1153 m	1146 m
$\nu_{38}$ , $\gamma$ -CH <sub>2</sub> antisymmetric rock	1058 (sh)	1068 m	1063 m	1069 m	1068 m	1068 m	1066 m	1068 m
$\nu_{20}$ , NH <sub>2</sub> wag	1012 Q, w	1009 s	1017 s	1003 s	996 s	1003 s	1017 m, sh	1021 m, sh
$\nu_{21}$ , ring deformation	948 w	939 w	944 m	940 w	991 s, sh	990 m, sh	996 m, sh	993 m, sh
$\nu_{22}$ , C-N in-plane bend	803 Q, sh	826 vw	846 vw	827 vw	938 w	940 w	943 w	944 w
$\nu_{23}$ , $\beta$ -CH <sub>2</sub> antisymmetric rock	770 vw	757 s, sh	767 vs	758 w, sh	848 vw	823 vw	no	824 vw
$\nu_{24}$ , ring deformation	545 sh	555 m, sh	565 m	554 m, sh	759 w	no	760 m, sh	no
$\nu_{25}$ , $\alpha$ -CH out-of-plane bend	537 Q, sh	539 m	552 m	554 m	553 w	553 w	565 m, sh	557 m, sh
$\nu_{26}$ , C-N in-plane bend	462 Q, sh	468 w, sh	469 w, sh	no	no	no	551 m	537 m
	455 P	448 w	455 w	447 w	448 w	448 w	456 m, sh	487 w, sh
								436 m, sh

<sup>a</sup> Taken from Ref. [10]. Abbrevs: v = very, s = strong, m = medium, w = weak, sh = shoulder and no = not observed.

<sup>b</sup>  $\nu_{14}$ (C-Nstr.),  $\nu_{34}$ ( $\beta$ -CH<sub>2</sub> antisym. twist),  $\nu_{35}$ ( $\alpha$ -CH out-of-plane bend) and NH<sub>2</sub> wag bands of CPA(gas) are not observed in the compounds studied.

Table 2c. Assignment and the wavenumbers for the CPA in the clathrates

Assignment <sup>a,b</sup>	CPA(IR) <sup>a,b</sup> (Gas)	Co-CPA-Ni-G G = Naphthalene	Cd-CPA-Ni-1,85G G = Naphthalene	Assignment <sup>a</sup>	CPA(IR) <sup>a</sup> (Gas)	Co-CPA-Ni-G G = Naphthalene	Cd-CPA-Ni-1,85G G = Naphthalene
v <sub>24</sub> , NH <sub>2</sub> antisym. str	3400 vw	3343 s	3339 s	v <sub>35</sub> , $\alpha$ -CH out-of-plane bend	1056 Q, m	no	no
v <sub>1</sub> , NH <sub>2</sub> symmetric stretch	3339 w	3283 m	3278 m	v <sub>36</sub> , v <sub>37</sub> , ring deformation	1012 Q, w	1010 s, sh	1017 s, sh
v <sub>2</sub> and v <sub>25</sub> , $\beta$ -CH <sub>2</sub> antisymmetric stretch	2968 vvs	2954 s	2956 s	v <sub>38</sub> , $\gamma$ -CH <sub>2</sub> antisymmetric rock	1003 sh	995 m, sh	992 m, sh
v <sub>3</sub> , $\alpha$ -CH stretch	2875 vvs	2912 w, sh	2911 w, sh	v <sub>20</sub> , NH <sub>2</sub> wag	948 w	956 w	956 w
v <sub>4</sub> , v <sub>26</sub> , $\beta$ -CH <sub>2</sub> symmetric stretch	2700 w	2869 m	2868 m		803 Q, sh	838 w	823 vw
v <sub>7</sub> , NH <sub>2</sub> deformation	1624 Q, s	1578 s	1578 s		708 Q, sh	no	no
v <sub>9</sub> , v <sub>30</sub> , $\beta$ -CH <sub>2</sub> deformations	1461 Q, s	1450 m	1450 m	v <sub>21</sub> , ring deformation	545 sh	567 m	567 m
v <sub>10</sub> , $\alpha$ -C-H in-plane bend	1356 s	1379 m	1389 m		537 Q, sh	552 m, sh	540 m, sh
v <sub>11</sub> , $\gamma$ -CH <sub>2</sub> symmetric wag	1322 vw	no	1327 vw		462 Q, sh	no	no
v <sub>14</sub> , C-N stretch	1204 (sh)	1211 w	1211 w	v <sub>22</sub> , C-N in-plane bend	455 P	452 w	444 w
v <sub>15</sub> , $\beta$ -CH <sub>2</sub> symmetric twist	1176 w	1169 w	1166 w				
		1153 m	1146 m				

<sup>a</sup> Taken from Ref. [10]. Abbrevs: v = very, s = strong, m = medium, w = weak, sh = shoulder and no = not observed.

<sup>b</sup> v<sub>14</sub>(C-N str.), v<sub>24</sub>( $\beta$ -CH<sub>2</sub> antisym. twist), v<sub>25</sub>( $\alpha$ -CH out-of-plane bend) and NH<sub>2</sub> wag bands of CPA(gas) are not observed in the compounds studied.

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

Host	Guest	<i>n</i>	Duration (approx.)
Co-CPA-Ni	Benzene	6.17	7 days
Cd-CPA-Ni		4.34	7 days
Co-CPA-Ni	Toluene	4.57	7 days
Cd-CPA-Ni		4.42	7 days
Co-CPA-Ni	<i>o</i> -Xylene	4.58	7 days
Cd-CPA-Ni		2.97	7 days
Co-CPA-Ni	<i>m</i> -Xylene	3.81	7 days
Cd-CPA-Ni		3.35	21 days
Co-CPA-Ni	<i>p</i> -Xylene	3.80	7 days
Cd-CPA-Ni		3.43	14 days
Co-CPA-Ni	1,2-Dichlorobenzene	3.56	21 days
Cd-CPA-Ni		2.60	21 days
Co-CPA-Ni	1,3-Dichlorobenzene	0.00	30 days
Cd-CPA-Ni		0.00	30 days
Co-CPA-Ni	1,4-Dichlorobenzene	0.00	30 days
Cd-CPA-Ni		0.00	30 days
Co-CPA-Ni	1,4-Dibromobenzene	0.03	21 days
Cd-CPA-Ni		0.00	21 days
Co-CPA-Ni	Naphthalene	1.15	6.5 months
Cd-CPA-Ni		1.85	6.5 months

pared with those of cyclopentylamine in the host complexes (Table 2). These upward frequency shifts are due to the hydrogen bonding between the (NH<sub>2</sub>) group and the guest molecules. Another notable feature is that N-H stretching vibrational frequencies in Cd-CPA-Ni-2G (G = *m*-xylene or *p*-xylene) and in the corresponding host complexes (Table 2b) are similar suggesting that there is no hydrogen bonding between NH<sub>2</sub> of the ligand and guest molecules.

As for the spectral changes of 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 not enclathrated guest (Table 4). Similar positive frequency shifts were observed for Hofmann-type clathrates and explained as being due to the presence of a weak hydrogen bond between  $\pi$  electrons located above and below the plane of the benzene ring and the ammonia molecules of the host lattice [5, 6]. Similar shifts have also been found for other members of Hofmann-type clathrates [3, 7, 8, 13]. Therefore, we may reasonably suggest that the frequency shifts in our compounds are due to the  $\pi$  electron donation from the guests to the hydrogen atoms of the NH<sub>2</sub> group of the ligand molecule which has a more electrophilic character caused by the coordination. The values of these shifts decrease 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)<sub>2</sub>C<sub>6</sub>H<sub>6</sub> (M = Mn or Cd, M' = Cd or Hg) [11], a doublet for our compounds and for M(cyclohexylamine)<sub>2</sub>Ni(CN)<sub>4</sub>.2benzene (M = Co or Cd)



Table 4. CH out-of-plane vibrational wavenumbers ( $\text{cm}^{-1}$ ) of the guests in the clathrates

Guest	Not enclathrated guest	Co-CHA-Ni <sup>g</sup>	Cd-CHA-Ni <sup>g</sup>	Co-CPA-Ni	Cd-CPA-Ni
Benzene <sup>a</sup>	670 (liquid)	688 s/684 vs 678 s	687 s	684 s 675 vs	683 s 675 vs
Toluene <sup>b</sup>	734 (liquid)	734 vs 728 s	734 vs 727 vs	737 vs 728 vs	735 s, sh 728 vs
1,2-dichlorobenzene <sup>b</sup>	748 (in CCl <sub>4</sub> and CS <sub>2</sub> )	748 vs	–	750 vs	750 vs
<i>o</i> -Xylene <sup>c</sup>	741 (liquid)	743 vs 755 vs	741 vs 752 vs	741 vs 758 w, sh	741 vs 757 w, sh
<i>m</i> -Xylene <sup>d</sup>	768 (liquid)	769 vs	767 vs	767 vs	767 vs
<i>p</i> -Xylene <sup>e</sup>	795 (liquid)	796 vs	795 vs	795 vs	796 vs
Napthalene <sup>f</sup>	782 (in CCl <sub>4</sub> and CS <sub>2</sub> )	–	786 vvs	796 vs 782 vs	785 vs

<sup>a</sup> Taken from Ref. [18].

<sup>b</sup> Taken from Ref. [19].

<sup>c</sup> Taken from Ref. [20].

<sup>d</sup> Taken from Ref. [21].

<sup>e</sup> Taken from Ref. [22].

<sup>f</sup> Taken from Ref. [23].

<sup>g</sup> Taken from Ref. [3].

Abbrs: v = very, s = strong, w = weak, sh = shoulder.

[3], Cd(pyrazine)M(CN)<sub>4</sub>.2C<sub>6</sub>H<sub>6</sub> (M = Cd or Hg) [14], M(NH<sub>3</sub>)<sub>2</sub>M'(CN)<sub>4</sub>.2C<sub>6</sub>H<sub>6</sub> (M = Mn or Cd, M' = Cd or Hg) [15] and M(tn)Zn(CN)<sub>4</sub>.2C<sub>6</sub>H<sub>6</sub> (M = Mn or Zn) [13], a singlet for M(NH<sub>3</sub>)<sub>2</sub>Ni(CN)<sub>4</sub>.2C<sub>6</sub>H<sub>6</sub> (M = Mn, Fe, Ni, Cu, Zn or Cd) [4,6] and Cd(4,4'-bipyridyl)M'(CN)<sub>4</sub>.2C<sub>6</sub>H<sub>6</sub> (M' = Cd or Hg) [16]. In the case of doublet or triplet features the splittings have been ascribed to crystal field effects (strong host-guest interactions) [4–6, 11, 12, 14–16]. 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 [16].

Based on the present data, it is not possible to determine the conformation of the ligand or guest molecules in the clathrate studies. As in the Hofmann-type and Hofmann-T<sub>d</sub>-type benzene clathrates, the relative orientation of the N–H bonds of cyclopentylamine with respect to the axis of the  $\pi$  cloud of guest must be the one most favorable for hydrogen bonding [17].

#### Selective absorption and separation of guest molecules

The phenomena described above 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) Infrared spectra show that when the host complexes are placed in a desiccator containing a mixture of benzene and toluene vapour with a mole ratio of 1/1, both benzene and toluene are sorbed. (ii) When the host compounds are placed in a desiccator containing a mixture of *o*-, *m*- and *p*-xylene mixture with mole ratios of 1:1:1, all isomers together are absorbed. (iii) Host complexes absorb 1,2-dichlorobenzene only from the 1,2-, 1,3- and 1,4-dichlorobenzene mixture with mole ratios of 1:1:1 (This result would also be expected from Table 3).

These results suggest that the host complex compounds presented here may be employed for selective absorption.

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 seven cycloalkylamines mentioned above are in progress.

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