



Infrared Spectroscopic and Gravimetric Studies on the Dicyclohexylaminocadmium(II) Tetracyanopalladate(II) Host-Aromatic Guest Systems

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Abstract

The host complex $\text{Cd}(\text{Cyclohexylamine})_2\text{Pd}(\text{CN})_4$ has been prepared in powder form. The spectral data suggest that the structure of this complex is similar to those of the Hofmann-dma-type hosts. The sorption processes of the aromatic guests (benzene, toluene, *o*-, *m*-, *p*-xylene, naphthalene, 1,2-, 1,3-, 1,4-dichlorobenzene and 1,4-dibromobenzene) in this host have been examined at room temperature by gravimetric and spectroscopic measurements. The desorption of the benzene guest against time has been measured. The host structure changes on inclusion of the guests and recovers after liberations. The host complex has been suggested as sorbents for selective absorption.

Introduction

Hofmann-type host complexes are formulated as $\text{ML}_2\text{M}'(\text{CN})_4$ (M = Mn, Fe, Co, Ni, Cu, Zn or Cd; M' = Ni, Pd or Pt; L=unidentate ligand). The structure of these hosts (Figure 1) consists of two dimensional polymeric layers formed from ML_2 cations and $\text{M}'(\text{CN})_4$ anions. The M' atom is bonded to four C atoms of the CN groups in a square-planar geometry. The 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 ligands 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, 2]. Of these, dimethylamine (dma) [1], cyclohexylamine [3] and cyclopentylamine [4] as ligands L, give a number of inclusion compounds with a selectivity very different from the Hofmann-type hosts. These hosts can include besides benzene a number of large aromatic guest molecules which have never been found enclathrated into Hofmann-type and the analogous hosts. Some of the inclusions compounds with dma 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 [1].

Keeping these unusual results in mind, we have been exploring the inclusion behaviours of the Hofmann-dma-type hosts with a series of cycloalkylamines and a variety of aromatic and aliphatic guests different in size and shape from those enclathrated in the Hofmann-type hosts [3, 4]. Until now, the sort of hosts we have examined are of the form $\text{ML}_2\text{Ni}(\text{CN})_4$, where, M = Co or Cd, L = cyclopentylamine [4], cyclohexylamine [3], cycloheptylamine [5], cyclooctylamine [5].

The host compounds of the above type reported to date have only been confined to a Ni atom in the square-planar environment [1, 3]. We have now prepared a host complex of the form $\text{Cd}(\text{cyclohexylamine})_2\text{Pd}(\text{CN})_4$ (abbr. Cd-CHA-Pd). It should be noted that several unsuccessful attempts have been made to synthesize the similar host complex of the form $\text{Co}(\text{cyclohexylamine})_2\text{Pd}(\text{CN})_4$. In this study, we report the sorption processes of the aromatic guests (benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,4-dibromobenzene and naphthalene) in

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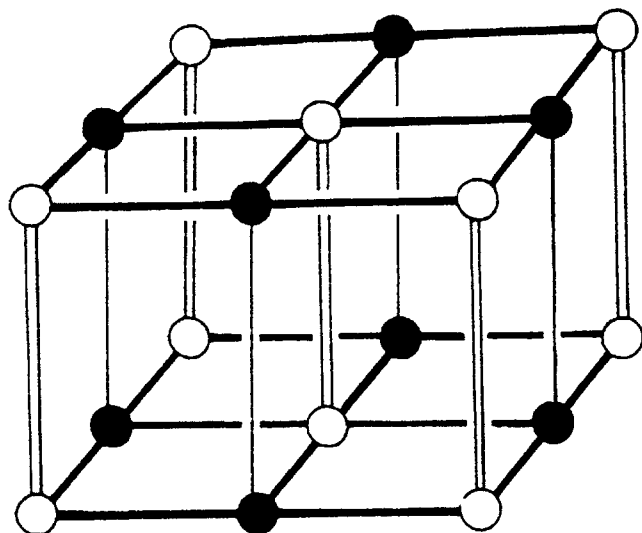


Figure 1. The model for the Hofmann-diam-type host structure (open circle: 6-coordinate M, solid circle: square-planar Ni, open column: an ambident ligand, thick line: CN bridge and thin line: edge of cavity).

the vapour phase at room temperature. The loss of benzene from the host compounds against time has been measured.

Experimental

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

$\text{Cd}(\text{C}_6\text{H}_{13}\text{N})_2\text{Pd}(\text{CN})_4$ was prepared by adding 3 millimole of CHA in solution in ethanol (ca. 20 ml) into 1 millimole of the Hofmann- H_2O -type hydrate $\text{Cd}(\text{H}_2\text{O})_2\text{Pd}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ which was prepared by the procedure similar to the $\text{Cd}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ complex of Kantarcı and Bülbül [3]. The host complex was obtained in quantitative yield. The freshly prepared complex was analysed for Cd and Pd (by atomic absorption method), C, H and N (by CHN analyser) with the following results (found C = 37.23/36.87, H = 5.31/5.03 and N = 16.36/16.12).

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

As seen below, the amount of the absorbed and liberated guest molecules were determined by weighing the sample at intervals, and graphs have been drawn as the increase (or decrease) of n against time. Accordingly, a number of spectra have been run for several n values ($n = 0.25, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75, 2.00, 2.25, \dots$). Of these, the spectra for $n = 2$ are given in Table 2. The spectra for $n < 2$ values correspond to the maximum n values attainable.

Infrared spectra of the compounds were recorded in the range $4000\text{--}400\text{ cm}^{-1}$ on a Mattson-1000 FT-IR spectrometer. The samples were prepared as mulls in nujol and fluorolube in a CsI cell.

Normal mode frequencies of CHA (in gas phase) have been calculated at the PW91/6-31G(d) level by using the package Gaussian 98 [6].

Results and discussion

For the comparison and discussion, the important spectral regions of CHA, $\text{Ni}(\text{CN})_4$, benzene and naphthalene species in different chemical states are shown in Figure 3 (as a representative illustration).

Before dealing with the inclusion and liberation of the guest moieties in the host complex, it is appropriate to elucidate the host structure on the basis of the available spectral data.

The assignment and the wavenumbers of the fundamental vibrations arising from the $\text{Pd}(\text{CN})_4$ and CHA species are given in Table 1 and Table 2, respectively. It will be convenient to divide the vibrations into two, arising from the $\text{Pd}(\text{CN})_4$ unit and from the CHA ligand.

$\text{Pd}(\text{CN})_4$ group vibrations

It is well known that the Pd atom in $\text{Pd}(\text{CN})_4$ is bonded in a square-planar geometry [7] and surrounded by the C ends of the CN ions. This fact suggests that the host framework of the complex compound $\text{Cd}(\text{CHA})_2\text{Pd}(\text{CN})_4$ also has a square planar $\text{Pd}(\text{CN})_4$ unit. In order to assign the bands attributable to the $\text{Pd}(\text{CN})_4$ ion in the spectra considered, we refer to the work of Jones [8] who presented vibrational data for the $\text{Pd}(\text{CN})_4$ ion which was treated as an isolated unit with D_{4h} symmetry. Thus these spectral data can be used as a reference to comment on vibrational changes when Cd–NC bonding takes place. The spectral data for the $\text{Pd}(\text{CN})_4$ groups in the compounds are given in Table 1, along with spectral data of the $\text{Pd}(\text{CN})_4$ anion. The assigned wavenumbers of the $\text{Pd}(\text{CN})_4$ units of the host complex studied are much higher than those for the isolated $\text{Pd}(\text{CN})_4$ ion (Table 1). Such frequency shifts have been observed for Hofmann-type host structures [9–13], and are attributed to the mechanical coupling of the internal modes of $\text{Ni}(\text{CN})_4$ with the M–NC vibrations. It follows that the N-termini of $\text{Pd}(\text{CN})_4$ unit are bound to a Cd atom in the host complex.

Cyclohexylamine vibrations

Up to now, there has been no extensive vibrational study of the cyclohexylamine molecule. However, the infrared and Raman spectral data for cyclopentylamine (CPA) in the gas phase [14], the infrared spectra of cyclohexylamine in the gas phase [15] and in dilute solutions ($\cong 0.2\text{ M}$) in nujol and fluorolube (as inert solvents) [3] have been reported. The proposed assignment of the infrared bands of CHA in the gas phase, in nujol (or fluorolube) and in the clathrate compounds were made taking into consideration the gas phase FT-infrared and Raman spectral data for cyclopentylamine (with a *gauche* orientation of the $-\text{NH}_2$ group) [14] that contain very similar chemical groups to those of cyclohexylamine. In order to facilitate the assignments, we have also observed the animations corresponding to the calculated frequencies by using HyperChem 7 [16]. As a whole, these assignments are in agreement with the calculated results (unpublished conformational studies have shown that isolated CHA should exist with a *trans* orientation of the $-\text{NH}_2$

Table 1. The wavenumbers of the Pd(CN)₄ unit of the Cd(CHA)₂Pd(CN)₄ complexes

Assignment ^a	Pd(CN) ₄ ⁻² a,b	Cd-CHA-Pd	Cd-CHA-Pd-2G G = Benzene	Cd-CHA-Pd-2G G = Toluene	Cd-CHA-Pd-2G G = <i>o</i> -Xylene	Cd-CHA-Pd-2G G = <i>m</i> -Xylene
A _{1g} , ν ₁	(2161)	–	–	–	–	–
B _{1g} , ν ₄	(2147)	–	–	–	–	–
ν ₈ , ν(CN), E _u	2142	2162 vs	2167 vs	2163 vs	2164 s	2162 vs
ν ₈ , ν(C ¹³ N), E _u	–	2137 sh	2141 w	2139 w	2139 sh	2139 w
Hot band	–	2122 w	2127 w	2130 w	2130 w	2130 w
ν ₉ , ν(PdC), E _u	503	490 w	492 w	490 w	491 w	493 w
A _{1g} , ν ₂	(430)	–	–	–	–	–
ν ₁₀ , δ(PdCN), E _u	393	402 vs	403 vs	401 vs	403 s	402 s
E _g , ν ₁₆	(295)	–	–	–	–	–
Assignment ^a	Pd(CN) ₄ ⁻² a,b	Cd-CHA-Pd-2G G = <i>p</i> -Xylene	Cd-CHA-Pd-2G G=1,2-dichlorobenzene	Cd-CHA-Pd-2G G=1,3-dichlorobenzene	Cd-CHA-Pd-0.4G G=1,4-dichlorobenzene	Cd-CHA-Pd-1.4G G=Naphthalene
A _{1g} , ν ₁	(2161)	–	–	–	–	–
B _{1g} , ν ₄	(2147)	–	–	–	–	–
ν ₈ , ν(CN), E _u	2142	2163 vs	2164 vs	2163 vs	2161 vs	2161 vs
ν ₈ , ν(C ¹³ N), E _u	–	2139 vw	2136 vw	2136 sh	2140 vw	2130 vw
Hot band	–	2130 w	2130 vw	2121 w	2121 sh	2121 vw, w
ν ₉ , ν(PdC), E _u	503	489 w	488 w, vw	490 vw	493 w	no
A _{1g} , ν ₂	(430)	–	–	–	–	–
ν ₁₀ , δ(PdCN), E _u	393	401 s	401 s	401 s	402 s	401 s
E _g , ν ₁₆	(295)	–	–	–	–	–

^aTaken from Ref. [8].

^bRaman frequencies are in brackets.

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

group). As is known, this sort of calculation overestimates the force constants, and hence the obtained vibrational frequencies are higher than the experimental ones. The usually applied correction factor of 0.9573 [17] does not allow us to reproduce precisely the experimental frequencies. The scaled frequencies (cm⁻¹) are given in Table 2a,b. This is due to the fact that the vibrational frequencies are derived from the harmonic approximation. Large amplitude (floppy) vibrational modes often exhibit significant anharmonicity that may increase errors in computed frequencies. In addition to anharmonicity, generally there might be coupling between vibrational modes which is not accounted for in the computational model.

The N–H stretching wavenumbers of the cyclohexylamine molecules in the complex compound are found to be lower than those in the gas phase or in the dilute solutions (Table 2a,b). 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 Cd atom. A metal dependent downward frequency shift is also observed for the NH₂ scissoring mode (Table 2a,b). Similar shifts have been measured in metal-coordinated aniline compounds [18–20].

Gravimetric results and spectral changes upon enclathration

When the host complex is 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

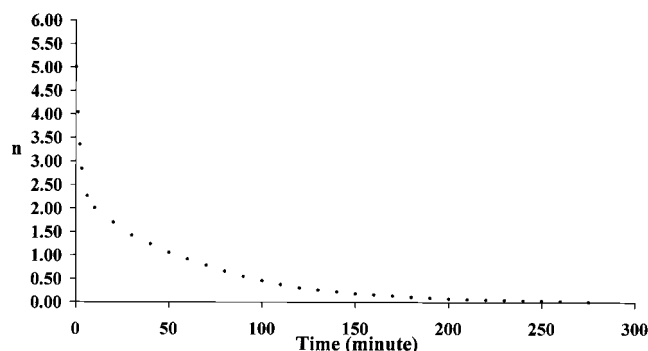


Figure 2. Decay of n (number of benzene molecules) against time for the Cd-CHA-Pd-Benzene system.

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 formula of the host complex, *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 ethanol solution products with a much lower number of guest molecules (in the range 0–0.4) than those in Table 3 are obtained. This is certainly due to liberation of guest molecules during drying of the products in open air). 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, 4].

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

Assignment ^a (gas) ^b	CPA (gas) ^b	CHA and fluorolube ^c	CHA (liquid) ^c	CHA (calculated)	CHA	Cu-CHA-Ni ^c	Cu-CHA-Pd G = Benzene	Cu-CHA-Ni-2G ^c G = Benzene	Cu-CHA-Pd-2G G = Toluene	Cu-CHA-Pd-2G
NH ₂ antisymm. str.	3400 vw	(3410 vw)	no	3383 s	3353 m	3405	3355 s	3353 s	3332 s	3332 m
NH ₂ symmetric str.	3339 w	(3336 m)	3336 w	3320 m	3280 m	3319	3292 m	3290 m	3277 m	3272 m
CH ₂ antisymm. str.	2968 vvs	(2970 vs)	2934 vs	no	no	2972	2971 w	2971 w	2966 w	2970 vw, sh
			2865 s	no	no	2939	2948 m, sh	2957 w, sh	no	no
CH-stretch		(2935 sh)	no	no	no	2905	2939 w, sh	2942 w, sh	2937 w	2943 m, sh
CH ₂ antisymm. str.			2922 s, sh	2934 vs	2926 vs	2903	2920 ms	2920 s	2921 s	2921 s
CH ₂ symmetric str.			2874 m, sh	2912 m, sh	2897 m, sh	2899	2905 m, sh	2907 m, sh	2906 m, sh	2906 m, sh
			2865 s	no	no	2887	2888 w, sh	2887 w, sh	no	2885 w, sh
	2875 vvs	(2882 s)	2859 s, sh	2858 ms	no	2885	2880 ms	2850 ms	2851 s	2850 m
	2700 w		1620 m	1616 ms	1598 ms	1623	1580 ms	1579 ms	1584 ms	1579 s
NH ₂ deformations	1624 s	(1472 sh)	1468 w, sh	1466 w	no	1465	1465 vw	1465 w	1464 w	1464 w, sh
CH ₂ deformations	1461 s	(1443 s)	1456 m	1453 ms	1449 ms	1450	1452 ms	1452 ms	1451 vs	1451 m
		(1380 vw)	1373 m	1377 m	1377 m	1378	1387 w, sh	1389 w	1389 w	1389 w
		(1350 vw)	1310 vw	no	1347 w	1341	no	1348 vw	no	1347 w
C-H in plane bend	1356 s		1258 w, bd	1309 w	1312 w, sh	1338	1312 vw	1312 vw	1310 w	1314 w
CH ₂ symm. wagg	1322 vwv		1230 w, sh	no	1281 w, sh	1286	1305 vw	1302 vw, sh	1304 vw, sh	no
			1206 w	1259 w	1259 w	1258	1277 vw	1272 vw	1275 vw	1273 vw
			1194 w	1203 w	1205 w	1243	1257 vw, sh	1256 w	1256 w	1256 w
CH ₂ antisymm. twist	1204 sh	(1188 bd)	1194 w	1170 w	1173 w	1098	1213 m	1215 m	1215 m	1213 w
C-N stretch	1184 sh		1098 w	1105 m	1102 m	1083	1169 m	1170 m	1170 m	1170 w
CH ₂ antisymm. twist	1102 sh		1036 w	1061 vw	no	1035	1114 m	1112 m	1117 m	1113 m
CH out-of-plane bend	1056 m	(1048 sh)	1010 vw	no	no	1004	1062 vw	1062 w	1063 w, sh	1064 vw
Ring deformation	1012 w	(1020 m)	985 vw	no	no	952	1000 vs	1002 vs	1016 vs	1001 vs
CH ₂ symmetric rock	948 w	(950 w)	926 vw	975 w	978 m	907	968 s	967 s	967 s	967 s
CH ₂ antisymm. rock			888 w	926 m	932 m	907	917 m	919 m	918 w	918 m
Ring breathing mode		(892 vs)	860 w, sh	893 s	898	881	889 s	890 s	889 s	889 ms
CH ₂ symmetric rock		(862 sh)	837 vw, sh	860 w, sh	862 m	862	875 m	874 w	878 w	876 w
Ring deformations		(834 sh)	800 w	843	840	844	840 w	841 w	842 w	843 w
NH ₂ wagging	803 sh		770 w	775 s	778 m	825	783 w	783 w	784 w	785 w
CH ₂ antisymm. rock	770 vw		no	no	no	762	no	769 vw	769 vw	772 vw
Ring deformation			545 sh	554 m	556 w	760	567 m	566 s	565 s	567 ms
		(538 m)	462 sh	466 w	464 w	528	532 s	533 s	531 s	532 s
			460 w	452 w	no	439	no	no	481 w	no
C-N in-plane-bend	460 w	(460 w)	460 vwv	452 w	no	430	449 w, sh	449 w	445 w, sh	448 w

^aTaken from Ref. [14].^bTaken from Ref. [16].^cTaken from Ref. [3].

Abbr.: v = very, s = strong, m = medium, w = weak, sh = shoulder, bd = broad, no = not observed. Raman frequencies are in parenthesis.

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

Assignment G = <i>o</i> -Xylene	Cd-CHA-Pd-2G G = <i>m</i> -Xylene	Cd-CHA-Pd-2G G = <i>p</i> -Xylene	Cd-CHA-Pd-2G G = 1,2-dichlorobenzene	Cd-CHA-Pd-2G G = 1,3-dichlorobenzene	Cd-CHA-Pd-2G G = 1,4-dichlorobenzene	Cd-CHA-Pd-0.41G G=Naphthalene	Cd-CHA-Pd-1.4G
NH ₂ antisymm. str.	3352 vw, 3334 m	3352 s, 3340 sh	3353 m, 3336 m	3352 w, 3334 m	3353 m, 3335 w	3353 m, 3334 w	3353 m, 3331 s
NH ₂ symm. str.	3290 sh, 3276 w	3290 m, 3276 sh	3290 m, 3279 m	3290 w, 3276 m	3290 m, 3276 w	3290 m, 3274 w	3290 w, 3275 m
CH ₂ antisymm. str.	2971 w	2971 w	2971 vw, sh	no	2971 w	2972 w	2971 w, sh
CH-stretch	no	2957 m, sh	no	2964 vw	2958 w, sh	2957 w, sh	no
CH ₂ antisymm. str.	2943 m, sh	2938 w, sh	2941 w, sh	2933 w, sh	2942 m	2942 m	no
CH ₂ symmetric str.	2921 vs	2921 vs	2921 vs	2921 s	2920 vs	2920 vs	2922 vs
	2903 m, sh	2906 m, sh	2907 m, sh	2906 m, sh	2906 m, sh	no	2907 m, sh
	2889 w, sh	2887 w, sh	no	no	no	no	no
	2851 s	2850 vs	2850 m	2851 s	2850 s	2849 s	2848 s
NH ₂ deformations	1579 m	1579 s	1579 s	1579 s	1578 vs	1577 m	1579 m
CH ₂ deformations	1466 w	1464 w, sh	1464 w, sh	1465 w	1477 w	1476 w	1463 w
	1450 vs	1457 vs	1451 m, sh	1458 vs	1451 s	1451 s	1451 s
	1385 w	1389 m	1388 w	1389 w	1388 m	1389 m	1390 m
C-H in-plane bend	no	no	no	no	no	no	no
CH ₂ symm. wag	1313 w	1311 w	1314 vw	1313 vw	1312 vw	1312 vw	1313 w
CH ₂ antisymm. wag	1304 vw	1304 vw, sh	no	no	1308 vw, sh	1306 vw, sh	1303 vw, sh
	1275 vw	1272 vw	1276 vw	1274 w	1274 vw	1274 w, sh	1273 m
CH ₂ antisymm. twist	1257 w	1257 w	1254 w	1252 m	1257 w	1257 w	1259 w, sh
	1215 w	1212 m	1213 m	1213 m	1213 m	1212 w	1213 m
C-N stretch	1171 w	1170 m	1172 m	1171 m	1171 w	1171 w	1167 w
CH ₂ antisymm. twist	1115 m	1113 m	1114 w	1115 w, sh	1112 m	1113 m	1115 m
CH out-of-plane bend	1065 w	1063 vw	1067 vw	1066 vw	no	1063 vw	1068 w
Ring deformation	1014 s	1002 vs	1005 s	1004 m	1002 vs	1002 vs	1019 vs
CH ₂ symm rock	967 m	968 m	968 m	967 m	968 m	967 m	968 s
CH ₂ antisymm rock	917 m	918 m	917 m	919 w	918 m	919 w	919 w
Ring breathing mode	890 m	890 m	890 m	891 m	890 m	890 m	894 m
CH ₂ symm rock	874 vw	876 w	876 w	880 vw	876 w, sh	876 w	882 w
Ring deformations	842 w	843 w	844 w	845 w	843 vw	842 vw	844 w
NH ₂ wag	784 vw	783 w	786 w	785 w	no	783 vw	784 s
CH ₂ antisymm rock	771 vw	no	no	no	no	772 m	770 w
Ring deformation	569 s	567 m	569 m	568 m	567 m	569 m	578 m
	532 s	534 m	531 m	532 m	532 m	532 m	539 m
	481 vw	no	469 vw	490 w	473 vw	473 vw	468 vw
C-N in-plane bend	449 w, sh	448 w	447 w, sh	439 w	448 w	447 w	445 w

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

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

Host	Guest	n	Duration (approx.)
Cd-CHA-Pd	Benzene	5.01	7 days
Cd-CHA-Pd	Toluene	3.50	24 days
Cd-CHA-Pd	<i>o</i> -Xylene	2.20	38 days
Cd-CHA-Pd	<i>m</i> -Xylene	2.11	41 days
Cd-CHA-Pd	<i>p</i> -Xylene	3.43	37 days
Cd-CHA-Pd	1,2-Dichlorobenzene	4.42	45 days
Cd-CHA-Pd	1,3-Dichlorobenzene	4.43	2 months
Cd-CHA-Pd	1,4-Dichlorobenzene	0.41	6 months
Cd-CHA-Pd	1,4-Dibromobenzene	0.00	30 days
Cd-CHA-Pd	Naphthalene	1.40	8 months

At this point, the structure of the compounds with n values higher than 2 may be questioned: are the guests simply adsorbed on the surface? If this were so then two sets of guest bands would be expected, one for the guest and one for the surface adsorbed species. In this context we report, one additional observation which lends support to this view: several Hofmann-type host complexes with different host moieties ($M(\text{NH}_3)_2\text{Ni}(\text{CN})_4$ ($M = \text{Co}, \text{Ni}$ or Cd)) were subjected to benzene (or toluene) vapour in equilibrium with its liquid phase in a desiccator at ambient conditions for a fortnight. Gravimetric measurements did not, however, indicate any increase in the weights of the host compounds. When the clathrates under study are left in the 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 Cd-CHA-Pd is illustrated in Figure 2 which plots the decrease of n against time. 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 with 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 Cd-CHA-Pd host, the band of $\text{Pd}(\text{CN})_4$ at 2162 cm^{-1} (Table 1) decreases in intensity and a corresponding new band at 2167 cm^{-1} grows in intensity. For $n = 2$, the former band (2162 cm^{-1}) disappears and the latter appears as a single band (2167 cm^{-1}). When n exceeds 2, another new band appears at 2172 cm^{-1} as a twin to the band at 2167 cm^{-1} . It is interesting to note that these twin bands of almost similar intensity are independent of the guest number for $n > 2$. Similar observations have also been noted for $M(\text{cyclohexylamine})_2\text{Ni}(\text{CN})_4$ ($M = \text{Co}$ or Cd) host complexes [3]. These spectral features may be due to some deviation from the square planar symmetry of the $\text{Pd}(\text{CN})_4$ 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 ($2172/2167 \text{ cm}^{-1}$) are unchanged with respect to the n values of 2 to 5, 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 [3]. Another conceivable suggestion may be that the primary ligand $\text{Pd}(\text{CN})_4$ behaves as a bidentate ligand (as $\text{NC-Pd}(\text{CN})_2\text{-CN}$) in the host framework. Similarly 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 [21]. It should be noted that these suggestions are tentative and possibly speculative but they are consistent with the present spectral data. Similar observations have been made for the other guest molecules (Table 1).

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 (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 π electrons located above and below the plane of the benzene ring and the ammonia molecules of the host lattice [9, 10]. Similar shifts have also been found for other members of Hofmann-type clathrates [12, 13, 18]. Therefore, we may reasonably suggest that the frequency shift in our compounds are due to the π electron donation from the guests to the hydrogen atoms of the NH_2 group of the ligand molecule which has a more electrophilic character caused by the coordination. The values of these shifts decrease in the order of increasing guest size.

Another notable feature of the CH out-of-plane vibration in benzene is that it appears as a triplet for $M(\text{en})M'(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ ($M = \text{Mn}$ or Cd , $M' = \text{Cd}$ or Hg) [32], a doublet for our compounds and for $M(\text{CHA})_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ ($M = \text{Co}$ or Cd) [3], $\text{Cd}(\text{pyrazine})M'(\text{CN})_4 \cdot \text{C}_6\text{H}_6$ ($M' = \text{Cd}$ or Hg) [33], $M(\text{NH}_3)_2M'(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ ($M = \text{Mn}$ or Cd , $M' = \text{Cd}$ or Hg) [34] and $M(\text{tn})\text{Zn}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ ($M = \text{Mn}$ or Zn) [35], and a singlet for $M(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ ($M = \text{Mn}, \text{Fe}, \text{Ni}, \text{Cu}, \text{Zn}$ or Cd) and $\text{Cd}(4,4'\text{-bipyridyl})M'(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ ($M' = \text{Cd}$ or Hg) [36]. In the case of doublet or triplet features the splittings have been ascribed to crystal field effects (strong host-guest interactions) [9–11, 32–36]. 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 [36]. Splitting has also been observed for toluene and *o*-xylene (Table 4). The band positions of benzene and toluene do not depend on the value of n ($n \leq 2$ 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 NH_2 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

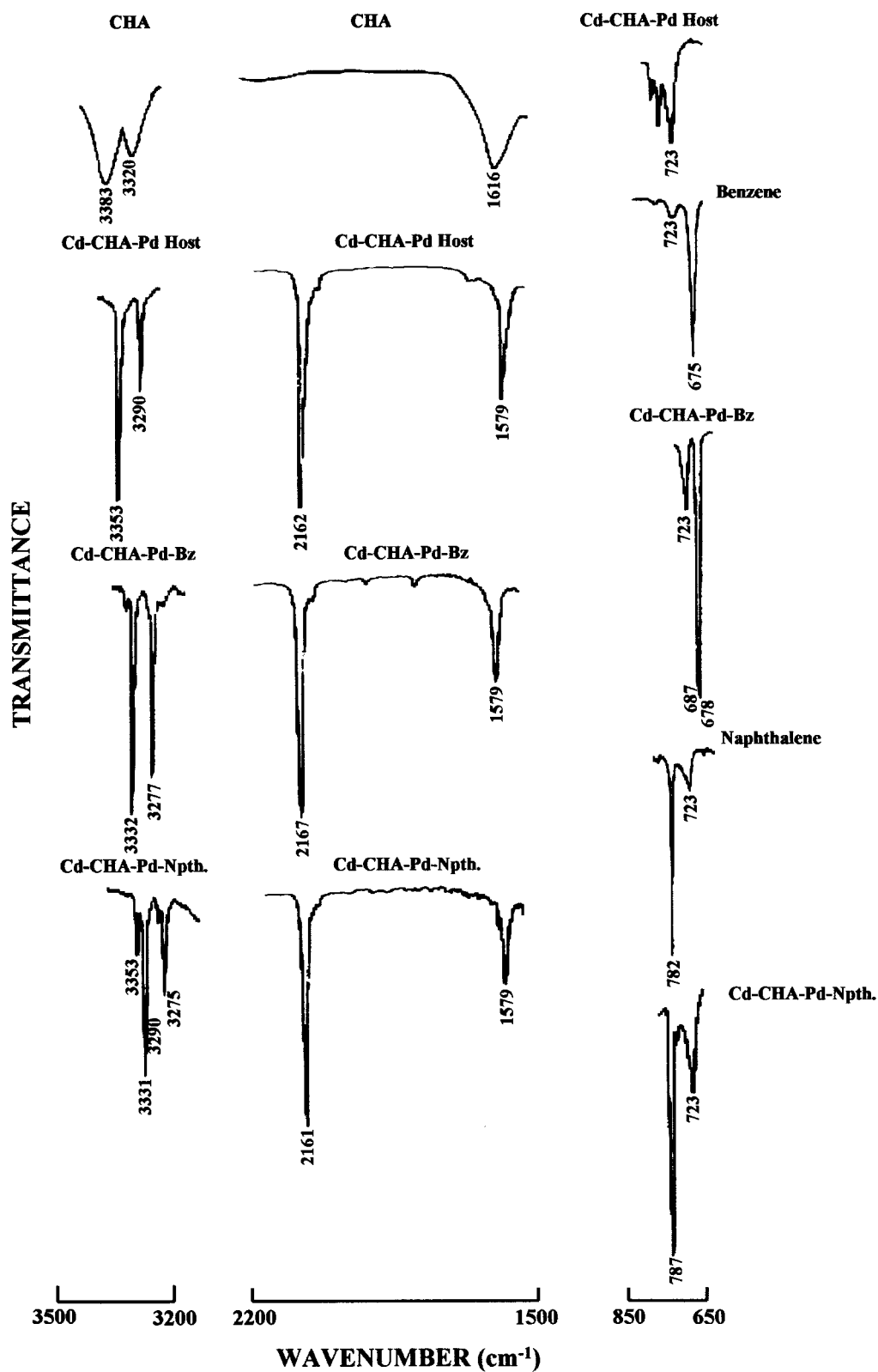


Figure 3. The important IR bands of CHA, Pd(CN)₄, benzene and naphthalene species in different chemical states related to Cd-CHA-Pd-Guest system (All compounds are in nujol).

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

Guest	Not enclathrated guest	Co-CHA-Ni ^g	Cd-CHA-Ni ^g	Cd-CHA-Pd
Benzene ^a	675 (in nujol)	688 s/684 vs 678 s	687 s	687 vs 678 vs
Toluene ^b	734 (liquid)	734 vs	734 vs	733 vs
<i>o</i> -Xylenec	741 (liquid)	728 vs	727 vs	728 vs
<i>m</i> -Xylene ^d	768 (liquid)	743 vs	741 vs	752 vs
<i>p</i> -Xylenee	795 (liquid)	755 vs	752 vs	753 vs
1,2-dichlorobenzene ^c	748 (in CCl ₄ and CS ₂)	769 vs	767 vs	768 vs
1,3-dichlorobenzene ^d	784 (in CCl ₄ and CS ₂)	796 vs	795 vs	750 vs
1,4-dichlorobenzene ^f	819 (gas)	748 vs	–	748 vs 759 vs
Napthalened	782 (in CCl ₄ and CS ₂)	–	–	785 vs
		–	–	818 m
		–	786 vvs	787 vvs

^aTaken from Ref. [22].

^bTaken from Ref. [23].

^cTaken from Ref. [25].

^dTaken from Ref. [26].

^eTaken from Ref. [28].

^fTaken from Ref. [27].

^gTaken from Ref. [3].

Abbr.: v = very, s = strong, m = medium, w = weak, sh = shoulder.

Hofmann-type benzene clathrates with amine and diamine ligands [32, 35].

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-Td-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 [37].

Selective absorption and separation of guest molecules

The phenomena just described imply the use 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–Pd 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 ($n = 5$). (ii) When the toluene clathrate Cd–CHA–Pd–To was placed in a desiccator containing benzene and toluene vapour as before, the benzene clathrate was obtained after two weeks ($n = 5$). (iii) The host complex absorbed *m*-xylene, *p*-xylene and *o*-xylene, from the *o*-, *m*- and *p*-xylene mixture with mole ratios of 1:1:1. The former two results suggest that the host complex compound 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 a series of cycloalkylamines (cyclopropylamine, cyclobutylamine, cyclopentyl amine, cyclohexylamine, cycloheptylamine, cyclooctylamine, cyclododecylamine, cyclohexyldiamine, cycloheptyl cyanide, cycloheptanecarbonitrile, cyclohexanecar-

bonitrile, cyclohexyl isocyanide, cyclohexyl isothiocyanate and cyclohexyl mercaptan) are in progress.

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