



Vibrational Spectroscopic Study on the Hofmann-Td-type 1,4-Dioxane Clathrates

Hofmann-Td–tipi Dioksan Klatratlarının Titreşim Spektroskopisi ile İncelenmesi

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ABSTRACT

Two new 1,4-dioxane-Td-type clathrates of the form $Cd(CPA)_2M(CN)_4 \cdot 2C_4H_8O_2$ (CPA= cyclopentylamine; M = Cd or Hg) have been prepared in powder form and their FT-IR (400-4000 cm^{-1}), FT-Raman (70-4000 cm^{-1}), far-IR (50-400 cm^{-1}) spectra, X-ray diffraction (XRD) and elemental analyses are reported. The spectral data suggest that the host frameworks of these compounds are similar to those of the Hofmann-Td-type benzene clathrates.

Key Words

Cyclopentylamine, 1,4-dioxane, FT-IR, FT-Raman, far-IR spectra, XRD, Hofmann-Td-type clathrates.

Öz

Öz formunda $Cd(CPA)_2M(CN)_4 \cdot 2C_4H_8O_2$ (CPA=siklopentilamin;M=Cd veya Hg) şeklindeki iki yeni 1,4-dioksan-Td tipi klatrat hazırlanmış ve bunların FT-IR (400-4000 cm^{-1}), FT-Raman (70-4000 cm^{-1}), uzak-IR (50-400 cm^{-1}) spektrumları, X-ışını kırınım dağılımı (XRD) ve elemental analizleri rapor edilmiştir. Spektral veriler, bu bileşiklerin konuk yapılarının Hofmann-Td tipi benzen klatratları ile benzer olduğunu ileri sürmektedir.

Anahtar Kelimeler

Cyclopentylamine, 1,4-dioksan, FT-IR, FT-Raman, far-IR spektrum, XRD, Hofmann-Td-tipi klatratları.

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INTRODUCTION

The structure of the Hofmann- T_d -type clathrates, $\text{Cd}(\text{NH}_3)_2\text{M}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ ($\text{M} = \text{Cd}$ or Hg), have already been determined [1]. In the host structure, M atom is tetrahedrally coordinated to the carbon atoms of the four cyanide ions, while the Cd atom is octahedrally surrounded by six nitrogen atoms, two are from the NH_3 ligands attached to the Cd atom in position trans to each other, the other four are from cyanide groups. The $\text{M}(\text{CN})_4$ groups are linked by the $\text{Cd}(\text{NH}_3)_2$ moieties to form a three-dimensional network. This framework provides two kinds of cavities, α and β , for the guest benzene molecules. The α -cavity is isostructural to that in the Hofmann-type clathrates with the shape of a rectangular box; β -cavity has the shape of a twisted biprism that is derived by rotating half of the rectangular box along the bisecting diagonal plane by ca. 90 degrees, as is schematically illustrated [1-3] in Figure 1.

In our previous paper [4], infrared spectroscopic studies on the $\text{M}(\text{cyclopentylamine})_2\text{Ni}(\text{CN})_4$ -aromatic guest systems ($\text{M} = \text{Co}$ or Cd) were described. Now, for the first time, two new Hofmann- T_d -type clathrates, $\text{Cd}(\text{cyclopentylamine})_2\text{M}(\text{CN})_4 \cdot 2\text{Dioxane}$ ($\text{M} = \text{Cd}$ or Hg) (abbr. Cd-CPA-M-2D) have been prepared in powder form. In this study, the FT-IR, FT-Raman, far-IR spectra and XRD of these compounds are reported. The spectral data are structurally correlated with those of the Hofmann- T_d -type clathrates $\text{Cd}(\text{NH}_3)_2\text{M}(\text{CN})_4 \cdot 2\text{Bz}$ ($\text{M} = \text{Cd}$ or Hg) [5], of which the structures are known [1, 2].

EXPERIMENTAL

$\text{Cd}(\text{II})$ chloride, $\text{Hg}(\text{II})$ chloride, potassium cyanide (KCN), cyclopentylamine and dioxane were purchased from commercial sources and used without further purification. The clathrate compounds were prepared according to the study reported previously [4].

Cd-CPA-Cd-2D: 2 millimoles (0.3288 g) of $\text{Cd}(\text{CN})_2$ and 3 millimoles of cyclopentylamine in 15 mL of dioxane were vigorously stirred for 5 days. The white precipitate was filtered, washed with ether, and kept in a desiccator containing dioxane vapor.

Cd-CPA-Hg-2D: Preparation was similar to the previous one using 1 millimole of $\text{Cd}(\text{CN})_2$ and 1 millimole of $\text{Hg}(\text{CN})_2$.

The freshly prepared compounds were also analyzed for C, H and N by LECO CHNS-932 analyzer with the following results (found % / calculated %):

$\text{Cd}(\text{C}_5\text{H}_9\text{NH}_2)_2\text{Cd}(\text{CN})_4 \cdot 2\text{C}_4\text{H}_8\text{O}_2$: C= 39.12/39.57, H= 5.67/5.86, N= 12.44/12.05.

$\text{Cd}(\text{C}_5\text{H}_9\text{NH}_2)_2\text{Hg}(\text{CN})_4 \cdot 2\text{C}_4\text{H}_8\text{O}_2$: C= 34.60/33.87, H= 5.01/5.21, N= 11.00/10.85.

The C, H and N analyses were carried out for all the compounds and found to fit the proposed formulas well. These analytical results are often poor for the complexes obtainable in powder form owing to

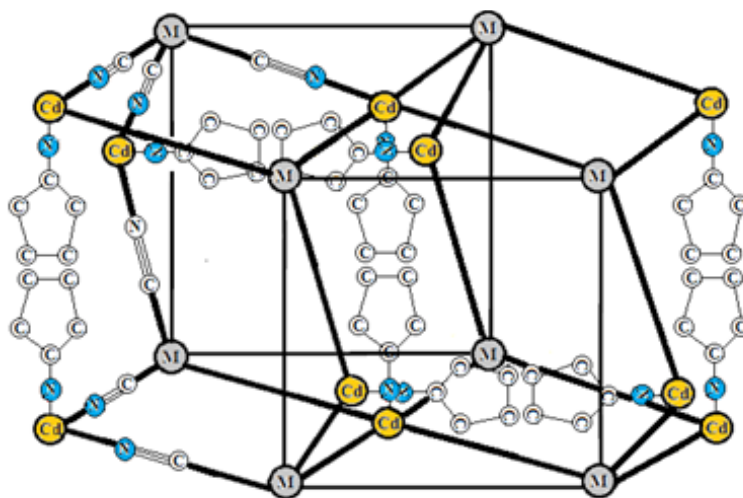


Figure 1. Schematic Hofmann- T_d -type Host Structure. Six-coordinate Cd; Tetrahedral M (Cd or Hg); cyanide bridges are shown with thick lines (N-C) between Cd and M. A β -cavity, with the hatched diagonal plane, is shown surrounded by four α -cavities.

partial decomposition. The experimental results are in agreement with the proposed formulas.

The clathrate compounds were prepared in saturated guest vapor as described in below. Infrared spectra of the compounds were recorded in the range 4000 and 200 cm^{-1} on Perkin-Elmer 1330 and Mattson 1000 FTIR spectrometers, which were calibrated using polystyrene and an indene/camphor/cyclohexane standard solution. The samples were prepared as mulls in Nujol and fluoroube (poly(chlorotrifluoroethylene)) between CsI plates. FT-Raman spectra were recorded using a Bruker RFS 100/S FT-Raman Spectrometer in the range 4000–50 cm^{-1} . The 1064 nm line, provided by a Nd: YAG air-cooled laser, was used as excitation line. A liquid nitrogen cooled Ge detector was used. The output laser power was set to 40–60 mW. The samples were prepared as mulls in nujol and hexachlorobutadiene between KBr pellets. Far-IR spectra of the nujol mulls between polyethylene windows of samples were recorded on a Perkin-Elmer System 2000 FT-IR Interferometer resolution (4 cm^{-1} resolution). The XRD pattern of the powder products were obtained on a Rigaku Rind 2200 diffractometer using Cu-K α radiation. The samples were loaded in a 0.3 mm glass capillary, which were rotated during the data collection.

RESULTS and DISCUSSION

The FT-IR, FT-Raman, far-IR spectra and XRD patterns of the $\text{Cd}(\text{CPA})_2\text{M}(\text{CN})_4 \cdot 2\text{Dioxane}$ ($\text{M} = \text{Cd}$ or Hg) clathrates are shown together Figure 2, 3, 4 and 5 respectively.

The spectral features of the compounds under study are found to be similar to each other, suggesting that they also have similar structural features. These similarities in spectra, furthermore, suggest that the symmetry restrictions of the compounds with different crystal symmetry possibilities are not effective. Therefore, the assignments were made by treating the CPA, $\text{M}(\text{CN})_4$ ions and the guest moieties as isolated units. The assignments and the wavenumbers of the observed bands arising from CPA, $\text{M}(\text{CN})_4$ and dioxane species are tabulated in Tables 1, 2 and 3, respectively, along with some relevant spectral data for comparison.

Cyclopentylamine Vibrations

Up to the time of writing, there have been a few studies concerning of the vibrational spectral data for the cyclopentylamine molecule. Of these the most relevant one for our purpose is that of Kalansinky et. al. [6] These authors have presented the infrared and Raman spectra of gaseous, liquid, and solid cyclopentylamine along with the infrared spectra of matrix-isolated samples. The spectral data of the CPA in the compounds studied are given in Table 1, together with spectral data for the CPA in the gas phase.

The N–H and C–N stretching frequencies of the CPA molecules in the compounds are found to be ca. 50 cm^{-1} lower than those of CPA in the gas phase [6]. These downward shifts may be explained as weakening of the N–H and C–N bonds resulting from the electron draining from the N atom on account of its coordination to the Cd atom in the octahedral arrangement.

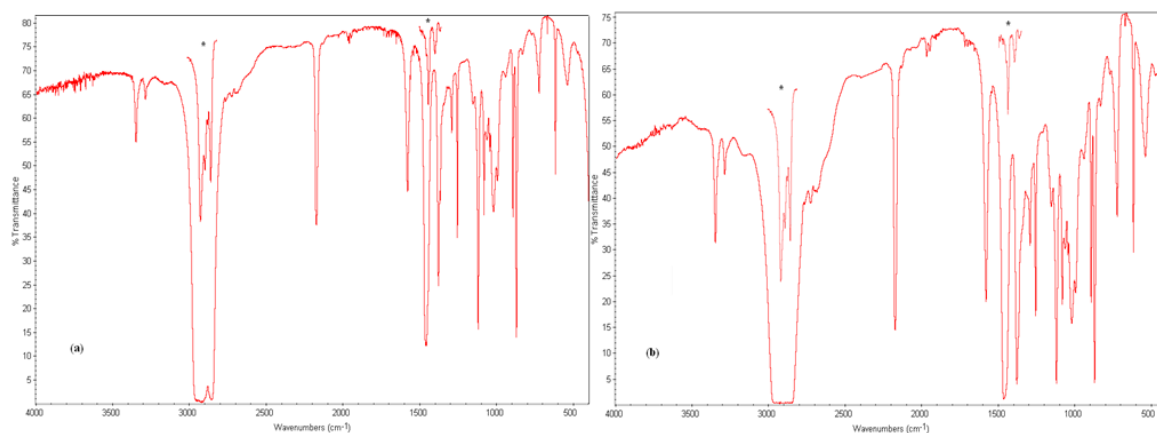


Figure 2. The FT-IR spectra of the Cd-CPA-Cd-2D (a) and Cd-CPA-Hg-2D (b) clathrates in nujol (*in poly(chlorotrifluoroethylene)-oil).

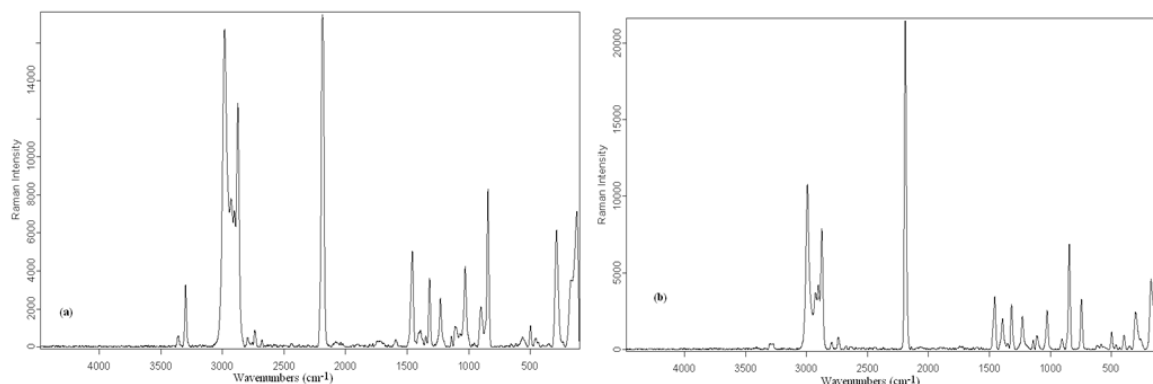


Figure 3. The FT-Raman spectra of the Cd-CPA-Cd-2D (a) and Cd-CPA-Hg-2D (b) clathrates.

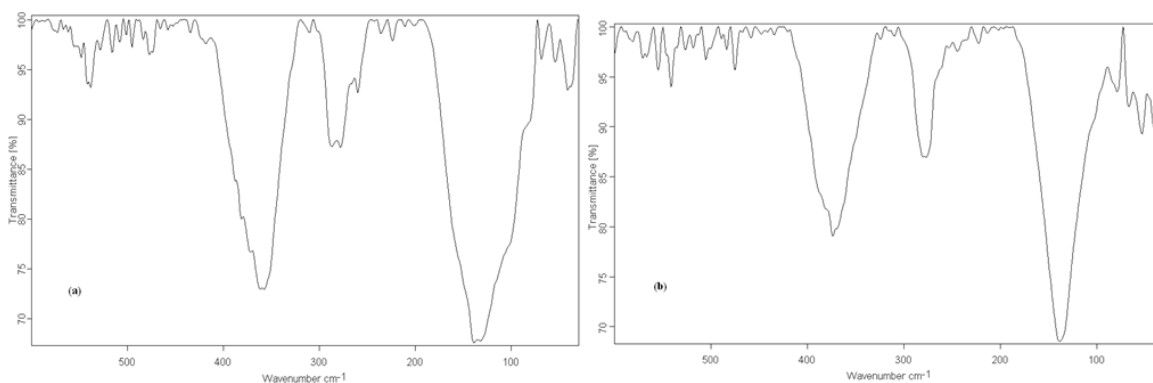


Figure 4. The far-IR spectra of Cd-CPA-Cd-2D (a) and Cd-CPA-Hg-2D (b) clathrates.

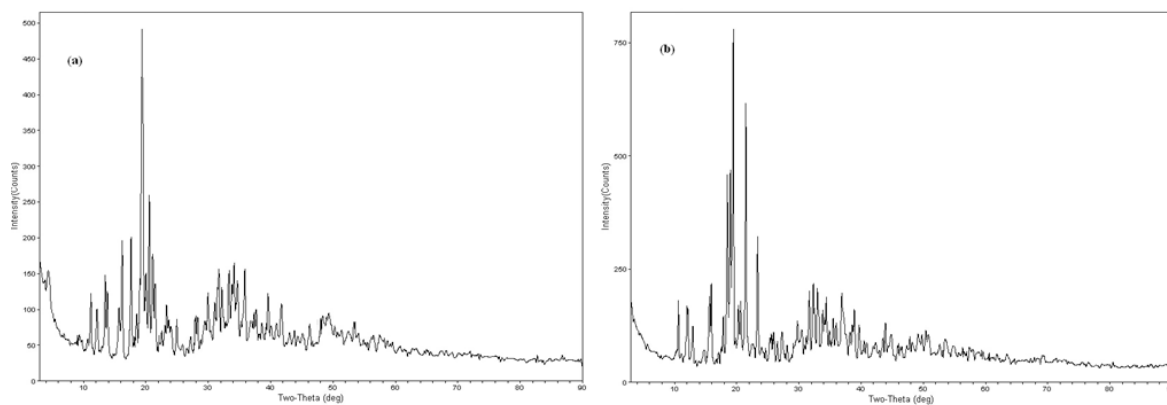


Figure 5. X-Ray powder diffraction (XRD) pattern of Cd-CPA-Cd-2D (a) and Cd-CPA-Hg-2D (b) clathrates.

Downward frequency shift is also observed for $\delta(\text{NH}_2)$ deformations vibrational (ν_7) mode (Table 1). Similar shifts have been observed in metal-coordinated aniline [7,8] and cyclohexylamine Hofmann-type clathrate compounds [9, 10].

$\text{M}(\text{CN})_4$ Group Vibrations

That in the host framework of the T_d -type clathrates [1,2] and the T_d -type host complexes [11] the metal atom M in $\text{M}(\text{CN})_4$ group is tetrahedrally surrounded

by the carbon ends of four CN ions suggests that the host structure of the present compounds have also tetrahedral $\text{M}(\text{CN})_4$ moieties. In assigning the bands attributable to the $\text{M}(\text{CN})_4$ (M= Cd or Hg) moieties, we refer to the vibrational data of $\text{K}_2\text{Cd}(\text{CN})_4$ and $\text{K}_2\text{Hg}(\text{CN})_4$ salts in the solid phase [12] (Table 2). The structural studies of these salts have shown that the K-NC distance is ca. 2.9 Å in $\text{K}_2\text{Cd}(\text{CN})_4$ [13] and $\text{K}_2\text{Hg}(\text{CN})_4$ [14], while this bond length is ca. 2.3 Å in T_d -type host structures [1,2,11]. Therefore, they can be used as references to

Table 1. Assignment and the vibrational wavenumbers (cm⁻¹) for the CPA in the Cd-CPA-M-2D (M=Cd or Hg) clathrates.

Assignment	Cyclopentylamine (CPA) ^a		Co-CPA-Ni-2Bz ^b		Cd-CPA-Ni-2Bz ^b		Cd-CPA-Cd-2D		Cd-CPA-Hg-2D	
	IR		Raman		IR	IR	IR	Raman	IR	Raman
	(Gas)	(Gas)	(Liquid)							
$\nu_{24'}$ NH ₂ antisymmetric stretch	3400 Q, vw	3410 vw	3360 w	3335 s	3337 s	3348 s	3358 vw	3347 s	3354 vw	
$\nu_{17'}$ NH ₂ symmetric stretch	3339 Q, w	3336 m	3310 p,m	3279 m	3278 m	3286 m	3299 m	3286 m	3299 m	
ν_2 and $\nu_{25'}$ β -CH ₂ antisymmetric stretch	2968 vvs	2970vs	2950 p,vs	2952 vs	2950 vs	2951 s,sh		2951s,sh		
$\nu_{3'}$ α -CH stretch				2907 w,sh	2916 m, sh	2919 m	2930 m	2919m	2926 m	
$\nu_{4'}$ $\nu_{26'}$ β -CH ₂ symmetric stretch	2875 vvs	2882s	2875 p,vs	2865 s	2861 s	2895w	2902 w	2893w	2902 w	
	2700 w		2863 sh	2725 w	2725 w	2756w	2736w	2760 w	2738w	
$\nu_{7'}$ NH ₂ deformation	1624 Q,s			1578 s,	1579 s	1579 s	1592w	1580 s	1592vw	
				1477 m						
$\nu_8, \nu_{29'}$ β -CH ₂ deformations		1472 Q,sh	1473 dp,sh							
$\nu_9, \nu_{30'}$ β -CH ₂ deformations	1461 Q,s	1443 Q,s	1445 dp,sh	1456 w	1451 w	1447 m,sh		1447m,sh		
		1380 vw	1382 dp,vw							
ν_{10} α -C-H in-plane bend	1356 s	1350 vw	1348 dp,vw	1378 m	1378 m	1378 m	1349vw	1378 m	1351vw	
ν_{11} γ -CH ₂ symmetric wag	1322 vw			1306 vw	1306 vw	1311 vw		1331 vw		
ν_{33} γ -CH ₂ symmetric wag		1226 bd	1225 p,bd				1230w		1229w	
$\nu_{14'}$ C-N stretch	1176 w	1188 bd	1174 p (bd)	1156 m	1151 m	1155 m	1140vw	1154w	1141vw	
$\nu_{34'}$ β -CH ₂ antisymmetric twist	1107 Q,m	1110 vw	1102 dp,w				1109 w		1109 w	
$\nu_{35'}$ α -CH out-of-plane bend	1056 Q,m	1048 Q,sh	1055 dp,sh	1066 m	1065 m	1063 m		1064 m		
$\nu_{36'}$ $\nu_{37'}$ ring deformation	1012 Q,w	1020 m	1025 dp,s	1014 s	1009 s	1018 s	1029m	1020 s	1027m	
$\nu_{16'}$ γ -CH ₂ symmetric rock	984 s	950 w	947 p,w	996 m,sh	9 9 3 m,sh	992 m		993 m		
$\nu_{38'}$ γ -CH ₂ antisymmetric rock	948 w			936 w	938 w	939 w		940 w		
$\nu_{39'}$ NH ₂ twist				no	919 vw	919 vw	901 w	921 vw	905 w	
$\nu_{17'}$ ring breathing mode		892 Q,vs	895 p,vs	892 w	894 w	no		no		
$\nu_{20'}$ NH ₂ wag	803 Q,sh			831 vw	829 vw	832 w		830 w		
$\nu_{41'}$ β -CH ₂ antisymmetric rock	770vw			770 w	771 vw	769 w,sh		752 w	745 w	
$\nu_{42'}$ ring deformation			601 dp,vw						617 w	
$\nu_{21'}$ ring deformation	545 sh	538 m	536 m	564 m, sh	556 m, sh	555 m,sh	560 w	549 m,sh	583 vw	
	537 Q,sh			532 m	535 m	539 m		538 m		
$\nu_{22'}$ C-N in-plane bend	460 Q,sh	460 w	457 p,w	481 vw	482 vw	474 w		474 w		
	455 P			455 m, sh	446 w,sh	446 w,sh		445 w, sh		
	356 w	355 vw	355 vw			362m,sh	287 m	381m,sh	300 m	
$\nu_{44'}$ ring twist	238 vw		238 vw			236w	177 m	244w	175 m	
$\nu_{45'}$ NH ₂ torsion	232 Q,w					222w		223w		

^{a,b}Taken from Refs. [6,4].

Abb: v, very; s, strong; m, medium; w, weak; bd, broad; sh, shoulder; no, not observed; p, polarized; dp, depolarized.

Table 2. Wavenumbers (cm⁻¹) of the M(CN)₄ group for the Cd-CPA-M-2D (M= Cd or Hg) clathrates.

Assignment ^[12]	K ₂ Cd(CN) ₄ ^a		K ₂ Hg(CN) ₄ ^a		Cd-(NH ₃) ₂ -Cd-2D ^b		Cd-(NH ₃) ₂ -Hg-2D ^b		Cd-CPA-Cd-2D		Cd-CPA- Hg-2D	
	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman
ν ₁ (CN) A ₁		2149		2149		2177 vs		2178vs		2180vs		2180vs
ν ₅ (CN) F ₂	2145		2146		2170vs	2170 m,sh	2170vs	2169s,sh	2172vs		2170vs	
Hot band									2142vw		2147vw	
ν ₂ (MC) A ₁		327		335		340w		337w		342w		350w
ν ₆ [n(MC)+δ(NCM)] F ₂	316		330		361s		368s		357vs		374vs	
ν ₇ [n(MC)+δ(NCM)] F ₂	250		235		271m	269m	257 m,sh		277m		276m	

^{a,b}Taken from Refs. [12,24].

Abb: v, very; s, strong; m, medium; w, weak; sh, shoulder.

account for the vibrational changes when the stiffer Cd-NC bonding takes place. The vibrational data for M(CN)₄ groups in the compounds are given in Table 2, together with the vibrational wavenumbers of K₂M(CN)₄ salts [12]. In Table 2 is also listed the wavenumbers of the infrared and Raman spectrum of the Cd(CN)₄ unit in Cd(NH₃)₂M(CN)₄·2Dioxane clathrate [5] for comparison. The assigned wavenumbers for the M(CN)₄ unite in the compounds studied appear to be much higher than those for M(CN)₄ ions in K₂M(CN)₄ salts (Table 2). Such frequency shifts have been observed for other Hofmann-T_d-type clathrates [5,15-17] and Hofmann-T_d-type host complexes [18,19], in which both ends of the CN group are coordinated and explained as the mechanical coupling of the internal modes of M(CN)₄ (M=Cd or Hg) with the Cd-NC vibrations. It follows that the N-ends of the M(CN)₄ units are also bound to a Cd atom in the clathrates understudied.

1,4-Dioxane Vibrations

Evidence that the molecule 1,4-dioxane has a chair conformation with the symmetry C_{2h} in the vapor and liquid phases has been provided by electron diffraction [20], Kerr constant measurements [21] and infrared and Raman spectral studies [22]. Moreover, X-ray diffraction [23] and vibrational studies [24] show that 1,4-dioxane has a chair conformation in the cadmium-nickel dioxane clathrate, Cd(NH₃)₂Ni(CN)₄·2C₄H₈O₂. Thus, the spectral bands attributable to the dioxane in our compounds are interpreted in terms of C_{2h} symmetry. The 36 fundamental vibrations divide into the following species: 10 A_g(R), 9A_u(IR), 8B_g(R) and 9B_u(IR).

The assignments and the frequencies of the vibrational bands arising from the dioxane species in the clathrate compounds are given in Table 3, along with the wavenumbers of dioxane in the vapour and liquid [22] and in the Cd(NH₃)₂Hg(CN)₄·2C₄H₈O₂ (M=Cd and Hg) clathrates [23] for comparison. Observations show that all the infrared bands of the dioxane guest molecules correspond closely in frequency and intensity suggestion that the dioxane molecules in the clathrate compounds are also in the chair conformation. Ongoing from free molecular state to clathrate, no notable frequency shifts in dioxane bands have been observed (Table 3). These findings suggest that the host-guest interactions in the clathrates are not significant. Similar suggestions have also been given for Hofmann-type and Hofmann-T_d-type dioxane clathrates [24-26].

Based on the spectral data presented here, it is not possible to determine the conformation and the orientation of the ligand or the guest 1,4-dioxane molecules in the clathrates. However, it may be speculated as the conformations of the ligand and the guest molecules must be the ones most favorable for hydrogen bonding [27].

The preceding discussion considered as a whole leads us the conclusion that the host lattice in our clathrates are similar to those of the other T_d-type clathrates [1, 2, 4, 5, 10, 15-17, 24, 26].

Table 3. Vibrational wavenumbers (cm⁻¹) of 1,4-dioxane in the Cd-CPA-M-2D (M=Cd or Hg) clathrates.

Assignment ^a	Liquid dioxane ^a		Cd-(NH ₃) ₂ -Cd-2D ^b		Cd-(NH ₃) ₂ -Hg-2D ^b		Cd-CPA-Cd-2D		Cd-CPA-Hg-2D	
	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman
$\nu_{21}(a_g, \nu_{20}(b_g))$		2968s		2979vs		2980vs		2982vs		2992vs
$\nu_{11}(a_u), \nu_{28}(b_u)$	2960vs		2981s		2980s		2968s		2966s	
$\nu_{21}(a_g, \nu_{21}(b_g))$		2856s		2860vs		2862vs		2874vs		2874vs
$\nu_{12}(a_u), \nu_{29}(b_u)$	2852vs		2860s		2860s		2863s		2862s	
$\nu_{22}(b_g)$		1459m,sh		1460m		1459m		1458m		1456m
$\nu_{30}(b_u)$	1454s		1452m		1454m		1455m		1454m	
$\nu_{13}(a_u)$	1446s,sh		1442m		1443m		1445m	1444m,sh	1445m	1443m,sh
$\nu_3(a_g)$		1444s		1445m		1445m				
$\nu_4(a_g)$		1397w		1398w		1396w		1393w		1392w
$\nu_{31}(b_u)$	1374m,sh		1377m		1377m		1381m		1384m	
$\nu_{14}(a_u)$	1366s		1367m		1367m		1367m		1367m	
$\nu_{23}(b_g)$		1335w								
$\nu_5(a_g)$		1305s		1305s		1307s		1318s		1318s
$\nu_{32}(b_u)$	1289s		1292s		1292s		1291s		1291s	
$\nu_{15}(a_u)$	1256s		1257s		1255s		1255s		1255s	
$\nu_{16}(a_u)$	1125vs		1117vs		1116vs		1118vs		1119vs	
$\nu_{24}(b_g)$		1217m		1217m		1217m				
$\nu_6(a_g)$		1128m		1126w		1126w				
$\nu_{25}(b_g)$		1110m		1100m		1098m		1109m		1110m
$\nu_{17}(a_u)$	1083s		1080s		1082s		1081s		1081s	
$\nu_{33}(b_u)$	1049s		1045s		1043s		1044s		1045s	
$\nu_7(a_g)$		1015s		1016s		1016s		1013m,sh		1013m,sh
$\nu_{34}(b_u)$	888s		891s		893s		892s		892s	
$\nu_{18}(a_u)$	874s		868vs		868vs		870vs		870vs	
$\nu_{26}(b_g)$		853m,sh		853w		854w				
$\nu_8(a_g)$		837vs		833vs		834vs		844vs		845vs
$\nu_{35}(b_u)$	614s		613m		617m		615m		615m	
$\nu_{27}(b_g)$		490m		488m		487m		498m		497m
$\nu_9(a_g)$		435m		446m		444m		456m		461m
$\nu_{10}(a_g)$		424m		424w		423w		424w		431w
$\nu_{19}(a_u)$	283m,sh		282m,sh		285m,sh		281m,sh		282m,sh	
$\nu_{36}(b_u)$	273s			272w		273w				

^{a,b}Taken from Refs. [22,24].

Abb: v, very; s, strong; m, medium; w, weak; sh, shoulder.

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