



Infrared Spectroscopic Study on the T_d -Type Clathrates: $Cd(Cyclohexylamine)_2M(CN)_4 \cdot 2C_6H_6$ ($M = Cd$ or Hg)

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Abstract

Two new title compounds have been prepared in powder form. Their spectral data are found to be consistent with the structure found in Hofmann- T_d -type clathrates.

Introduction

The structure of the Hofmann- T_d -type clathrates, $Cd(NH_3)_2M(CN)_4 \cdot 2C_6H_6$ ($M=Cd$ or Hg) (abr. $Cd-NH_3-M-2Bz$) have already been determined by single crystal x-ray diffraction methods; the former is monoclinic with the space group $C2/c$ (C_{2h}^6) [1], the latter being triclinic with the space group $P\bar{1}(C_1)$ [2]. In the host structures of these compounds, which are substantially isostructural, the M atom is tetrahedrally coordinated to the carbon atoms of the four cyanide groups, while the Cd atom is octahedrally surrounded by six nitrogen atoms, two are from the two NH_3 ligands attached to the Cd atom in positions *trans* to each other, the other four are from cyanide groups. The $M(CN)_4$ groups are linked by the $Cd(NH_3)_2$ 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; the β -cavity has a shape of a twisted biprism that is derived by rotating the half of a rectangular box along the bisecting diagonal plane by ca. 90° (Figure 1) [3]. The volume of the β -cavity is approximately the same as that of the α -cavity, unless distortion occurs to a considerable extent. In the case of considerable distortion of the $CdM(CN)_4$ framework, substantial symmetry alterations may be expected resulting in changes in the spectral activities [1–3].

Several novel T_d -type host structures have been developed from that of Hofmann- T_d -type clathrates described above by replacing two NH_3 ligands facing each other in the interlayer space by a pair of other unidentate ligands or an ambidentate ligand. When a bulky ligand or a ligand with bulky substituent is introduced into the host structure the ligand occupies the cavity partly or wholly in place of a guest. The number of guest molecules in the general formula may vary stepwise from 2, $3/2$, 1, $1/2$ to 0 according to the number of cavities (0, 1, 2, 3

or 4) occupied [4]; e.g., in the host structure of the 1,2-diaminopropane- T_d -type clathrate, $Cd(pn)Cd(CN)_4 \cdot 1.5G$, a pair of methyl groups are thought to occupy a cavity instead of a guest molecule similar to the Hofmann- pn -type clathrates [5]. Other examples are $Cd(pyrazine)M(CN)_4 \cdot C_6H_6$ ($M = Cd$ or Hg) [6], $Cd(Aniline)_2Cd(CN)_4 \cdot 1/2Aniline$ [7], $Cd(pyridine)_2Cd(CN)_4$ ($n = 0$) [8], and $ML_2M'(CN)_4$ ($M = Mn$ or Zn ; $M' = Zn$, Cd or Hg ; $L = pyridine$, α -, β - or γ -picoline) ($n = 0$) [9].

In our previous paper [10], gravimetric and infrared spectroscopic studies on the $M(cyclohexylamine)_2Ni(CN)_4$ -aromatic guest systems were described. Now, for the first time, two new Hofmann- T_d -type clathrates, $Cd(cyclohexylamine)_2M(CN)_4 \cdot 2C_6H_6$ ($M=Cd$ or Hg) (abr. $Cd-CHA-M-2Bz$) have been prepared in powder form. In this study, infrared spectra of these compounds are reported. The spectral data of these compounds are structurally correlated with those of the T_d -type $Cd(NH_3)_2M(CN)_4 \cdot Bz$ ($M=Cd$ or Hg) clathrates, of which the structures are known [1, 2]

Experimental

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

The clathrate compounds were prepared as follows: $Cd-CHA-Cd-2Bz$: 2 millimoles of $Cd(CN)_2$ and 2 millimoles of cyclohexylamine in 15 mL of benzene were vigorously stirred for five days. The white precipitate (powder) was filtered and washed with ether three times, and dried in open air and kept in a desiccator containing benzene vapour.

$Cd-CHA-Hg-2Bz$: The preparation was similar to the previous one using 1 millimole of $Cd(CN)_2$ and 1 millimole of $Hg(CN)_2$. The freshly prepared compounds were analyzed for Cd , Hg (by atomic absorption) and N (by the Kjeldahl method) with the following results (found %/calculated %).

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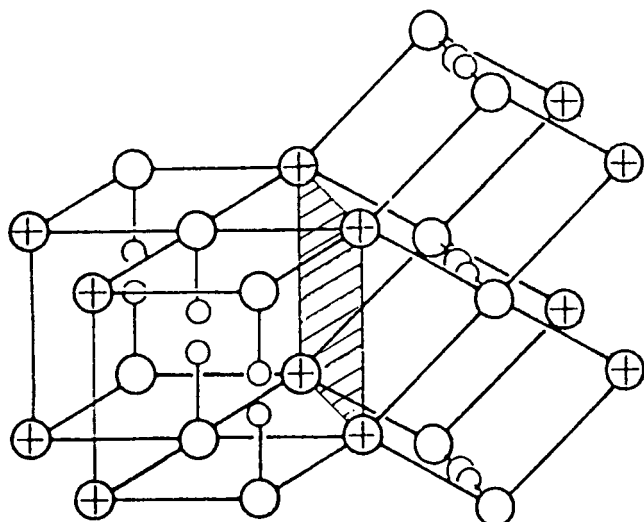


Figure 1. Schematic Hofmann- T_d -Type Host Structure. Large open circle, six-coordinate Cd; crossed circle, tetrahedral M (Cd or Hg); small circle, N of NH_3 ; cyanide bridges are shown with thick lines between Cd and M. A β -cavity, with the hatched diagonal plane, is shown surrounded by four α -cavities.



$$Cd = 32.45/32.89, N = 12.22/12.30$$



$$Cd = 14.42/14.57, Hg = 25.87/26.00, N = 10.70/10.89.$$

Infrared spectra were recorded in the range 4000–200 cm^{-1} on Perkin-Elmer 1300 and Mattson 1000 FTIR spectrometers, which were calibrated using polystyrene and indene. The samples were prepared as mulls in nujol and in poly(chlorotrifluoroethylene) between CsI plates.

Results and discussion

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 [11–13]. Therefore, the assignment was made by treating the CHA, $M(CN)_4$ and the guest moieties as isolated units. The assignments and the wavenumbers of the observed bands arising from CHA, $M(CN)_4$ and benzene species are tabulated in Tables 1, 2, and 3, respectively, along with some relevant spectral data for comparison.

Cyclohexylamine vibrations

Up to the time of writing, there have been no studies concerning the vibrational spectral data for the CHA molecule.

Because of the possibility of low symmetry for the molecule, the assignments of the spectral bands were made in terms of characteristic group frequencies. The tentative assignments of the fundamental bands of CHA observed in the spectra of the compounds under study are partly based on the assignments of the infrared and Raman spectra of CHA in the liquid and vapour states of cyclobutylamine studied previously [14]. In order to assign and interpret the bands attributable to the CHA ligand in the clathrate compounds, we refer to the spectral data for the isolated (non-interacting) CHA molecule. Hence, the cyclohexylamine molecule in a dilute solution (ca. 0.2 molar of CHA) in an inert solvent (nujol or poly(chlorotrifluoroethylene)) can be treated as an isolated entity (close to the gas phase) and thus used as reference to comment on vibrational changes when Cd-CHA bonding takes place. The spectral data of the compounds studied are given in Table 1, together with the spectral data for liquid CHA and CHA in solution in nujol and in poly(chlorotrifluoroethylene) and in the $Cd(CHA)_2Ni(CN)_4 \cdot 2Bz$ clathrate for comparison.

The N–H and C–N stretching frequencies of the cyclohexylamine molecules in the compounds are found to be lower than those of cyclohexylamine in solution (Table 1). 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 in the $-NH_2$ unit on account of its coordination to the Cd atom in the octahedral arrangement and the hydrogen bonding to the π electrons of the guest benzene ring (see below). A downward frequency shift is also observed for the NH_2 scissoring vibrational mode (Table 1). Similar shifts have been observed in metal-coordinated aniline compounds [15, 16]. Based on the spectral data presented here, it is not possible to determine the conformation of the ligand and the orientation of the guest benzene molecules in the clathrates. However, it may be speculated that, as in the Hofmann-type clathrates, the relative orientation of the N–H bonds with respect to the axis of the π cloud of benzene must be the one most favourable for hydrogen bonding [17].

$M(CN)_4$ vibrations

The fact that in the host framework of the T_d -type clathrates [1, 2] and the T_d -type complexes [18] the metal atom M in the $M(CN)_4$ group is tetrahedrally surrounded by the carbon ends of four CN ions suggests that the host structure of the present compounds also have tetrahedral $M(CN)_4$ moieties. In assigning the bands attributable to the $M(CN)_4$ ($M=Cd$ or Hg) species, we refer to the vibrational data of $K_2Cd(CN)_4$ and $K_2Hg(CN)_4$ salts in the solid phase [19](Table 2). The structural studies of these salts have shown that the K–NC distance is ca. 2.9 Å in $K_2Cd(CN)_4$ [20] and $K_2Hg(CN)_4$ [21], while this bond length is ca. 2.3 Å in T_d -type host structures [1, 2, 18]. Therefore, the spectral data of these salts may be used as references to account for the vibrational changes when the stiffer Cd–CN 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 $K_2M(CN)_4$ ($M = Cd$ or Hg) salts [19]. Table 2 also lists the wavenumbers of the infrared spectra of the $M(CN)_4$ unit

Table 1. The infrared wavenumbers (cm^{-1}) of CHA in Cd-CHA-M-2Bz (M = Cd or Hg) clathrates and related compounds*

Assignment ^a	CHA (liquid) ^a	CHA in nujol and PCI-3F-ethylene ^a	Cd-CHA-Ni-2Bz ^a	Cd-CHA-Cd-2Bz	Cd-CHA-Hg-2Bz
NH ₂ antisym.str	3353 m	3383 s	3332 s	3334 s	3333 s
NH ₂ sym. str	3280 m	3320 m	3277 m	3228 m	3277 m
CH ₂ antisym. str	–	–	2972 w	2972 w	2973 w
CH ₂ antisym. str	–	–	2948 w, sh	2949 w, sh	2948 w, sh
CH ₂ antisym. str	–	–	2937 w, sh	2937 w, sh	2937 w, sh
CH ₂ sym. str	2926 vs	2934 vs	2919 vs	2920 vs	2919 vs
CH ₂ sym. str	2897 m, sh	2912 m, sh	2905 m, sh	2907 m, sh	2906 m, sh
CH ₂ sym. str	–	–	2888 w, sh	2888 w, sh	2887 w, sh
CH str	2853 ms	2858 ms	2851 vs	2852 vs	2851 vs
NH ₂ scissoring	1598 ms	1616 ms	1584 ms	1581 ms	1581 ms
	1568 w, sh	1574 w	No		
CH ₂ deform.	–	1466 w	1464 w	1465 w	1465 w
CH ₂ deform	1449 ms	1453 ms	1451 vs	1452 vs	1452 vs
CH ₂ deform	–	–	1443 w, sh	1443 w, sh	1442 w, sh
CH bending	1377 m	1377 m	1389 w, sh	1388 w, sh	1388 w, ssh
	1347 w				
NH ₂ wagging	1312 w, sh	1309 w	1310 w	1312 w	1312 w
NH ₂ wagging	1281 vw, sh	–	1304 vw, sh	No	No
CH ₂ wagging	1281 w	–	1275 vw	1267 w	1267 w
CH ₂ wagging	1259 w	1259 w	1256 w	1261 vw, sh	1261 vw, sh
CH ₂ wagging	1205 w	1203 w	1215 m	1216 m	1216 m
Ring-deform.	1173 w	1170 w	1170 m	1160 m	1160 m
Ring deform.	1152 w	1148 w	1155 w, sh	No	1149 w
CH ₂ twisting	1102 m	1105 m	1117 m	1120 m	1120 m
CH ₂ twisting	1092 m	1090 m	1097 w	1096 w	1096 w
CH ₂ twisting	–	1061 vw	1063 w, sh	1070 m, sh	1069 m, sh
C-N str	1038 w	1036 m	1039 s	1041 m, sh	1049 m, sh
C-N str	–	–	1016 vs	1016 vs	1018 vs
Ring breathing	978 m	975 w	965 s	964 s	964 s
Ring breathing	–	–	No	No	No
NH ₂ twisting	932 m	926 m	918 w	921 s	922 w
Ring deformation	898	893 s	889 s	890	892 s
C-H bending	862 m	860 w, sh	878 w	882 w	881 w
CH ₂ rocking	840	843	842 w	847 w	848 w
CH ₂ rocking	778 m	775 s	784 w	786 w	787 w
Ring deformation	–	–	769 vw	773 vw	772 vw
CH ₂ rocking	600 vw	–	593 vw, sh	No	No
CH ₂ rocking	–	–	565 s	565 m	566 m
CH ₂ rocking	556 w	554 m	531 s	No	No
Ring C-N bending	464 w	466 w	482 w	482 w	482 w
	–	452 w	445 w, sh	442 w, sh	443 w, sh

^aTaken from Ref. [10].

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

in the Cd(NH₃)₂M(CN)₄·2C₆H₆ (M=Cd or Hg) clathrates [22] for comparison.

The assigned wavenumbers for the M(CN)₄ moiety in the compounds studied appear to be much higher than those for the M(CN)₄ ion in K₂M(CN)₄ salts (Table 2). Such frequency shifts have been observed for other Hofmann-T_d-type clathrates [8, 9, 11–22] and Hofmann-T_d-type host complexes [8, 9], 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 [6, 8, 9, 11–13, 22, 24, 25].

Benzene vibrations

The assignments and the frequencies of the vibrational bands arising from the benzene observed in the spectra of Cd-CHA-M-2Bz (M=Cd or Hg) compounds are given in Table 3, along with the wavenumbers of the benzene in the liquid phase [23] and in the Cd(NH₃)₂M(CN)₄·2C₆H₆ (M=Cd or Hg) [22] and Cd(CHA)₂Ni(CN)₄·2C₆H₆ [10] clathrates for comparison. The most structurally informative spectral features are the following.

The CH out-of-plane mode (A_{2u}) in the spectra of the clathrates are found to be shifted to higher frequency

Table 2. Cyanide group vibrational wavenumbers (cm^{-1}) in $\text{Cd}(\text{CHA})_2\text{Cd}(\text{CN})_4 \cdot 2\text{Bz}$ and $\text{Cd}(\text{CHA})_2\text{Hg}(\text{CN})_4 \cdot 2\text{Bz}$ clathrates*

Assignment ^a	$\text{K}_2\text{Cd}(\text{CN})_4^a$	$\text{K}_2\text{Hg}(\text{CN})_4^a$	$\text{Cd-NH}_3\text{-Cd-2Bz}^b$	$\text{Cd-NH}_3\text{-Hg-2Bz}^b$	Cd-CHA-Cd-2Bz	Cd-CHA-Hg-2Bz
$\nu_1(\text{CN}) A_1$	(2149)	(2149)	(2178) vs	(2178) vs-	no	no
$\nu_5(\text{CN}) F_2$	2145	2146	2165 vs, (2165) m	2168 vs, (2167) m	2182 vs, 2174 m, sh	2181 vs, 2173 m, sh
Hot band	–	–	2154 vw	2155 vw	no	no
$\nu_5(^{13}\text{CN})$	–	–	2135 vw	2136 w	2139 vw	2138 vw
$\nu_2(\text{CN}) A_1$	(327)	(335)	(341) vw-	(341) vw	no	no
$\nu_6 + \nu_7$	–	–	610 w	608 w	no	no
$\nu_6[\nu(\text{MC}) + \delta(\text{NCM})]F_2$	316		360 s	358 s	370 s	371 s

* Raman bands are in parentheses.

^{a,b} Taken from Refs [19] and [22], respectively. no = not observed, v = very, s = strong, m = medium, sh = shoulder.Table 3. The vibrational wavenumbers (cm^{-1}) of benzene in the Cd-CHA-M-2Bz (M = Cd or Hg) clathrates and related compounds*

Assignment ^a	Liquid benzene ^b	$\text{Cd-NH}_3\text{-Cd-2Bz}^c$	$\text{Cd-NH}_3\text{-Hg-2Bz}^c$	Cd-CHA-Ni-2Bz^d	Cd-CHA-Cd-2Bz	Cd-CHA-Hg-2Bz
$\nu_8 + \nu_{19}$	3075	3064 m	3062 w	3069 w	3071 w	3072 w
$\nu_{20}E_{1u}$	3073	3080 m	3076 m	3088 m	3090 w	3091 w
$\nu_{13}B_{1u}$	3062	3028 m	3024 m	3033 m	3035 m	3035 m
ν_2A_{1g}	(3059)	(3060)	((3061) m)	no	no	no
ν_7E_{2g}	(3046)	(3040)	(3040 w)	no	no	no
$\nu_5 + \nu_{17}E_{1u}$	1955		1966 w	1967 w	1967 w	1967 w
$\nu_{10} + \nu_{17}$	1815	–	1823 vw	1824 w	1824 w	1825 w
ν_8E_{2g}	(1596)	(1580 w)	(1581 m)	no	no	no
$\nu_{19}E_{1u}$	1479	1477 m	1480 s	1476 s	1477 s	1476 s
$\nu_{14}E_{2u}$	1309	–	–	1305 vw	1305 vw	1305 vw
ν_9E_{2g}	(1178)	(1174 m)	(1174 m)	no	no	no
$\nu_{15}B_{2u}$	1149	1145 sh	1145 sh	no	no	no
$\nu_{18}E_{2u}$	1036	1032 w	1035 m	1035 vw	obs	obs
ν_1A_{1g}	(992)	(989 vs)	(987 vs)	no	no	no
$\nu_{10}E_{1g}$	(849)	(854 w)	855 w vs	no	no	no
$\nu_{11}l_{2u}$	670	698 s, 689 vs	701 s, 688 vs	687 s	686 vs	687 vs
ν_6E_{2g}	(606)	(604 m)	(605 m)	no	obs	obs

* Raman bands are in parentheses.

^{a,b,c,d} Taken from Refs [26, 23, 25, 10] respectively. v = very, s = strong, m = medium, w = weak, no = not observed, obs = obscured by ligand bands.

(681 cm^{-1}) (Table 3) from that of liquid benzene (670 cm^{-1}). Similar positive frequency shifts were observed for Hofmann- T_d -type [11–13, 22] and Hofmann-type clathrates [15] and explained by the presence of a weak hydrogen bond between the π electrons located above and below the plane of the benzene ring and the ammonia molecules of the host lattice. Therefore, we may reasonably suggest that the frequency shifts in our clathrate compounds are due to the π electron donation from the benzene ring to the hydrogen atoms of the NH_2 group of CHA which has a more electrophilic character caused by the M–N coordination.

Another notable feature of the out-of-plane mode (A_{2u}) is that it appears as a very intense single band at ca. 686 cm^{-1} in the infrared spectra of the clathrate compounds (Table 3). A similar single band was observed for $\text{Cd}(4,4'\text{-bipyridyl})\text{M}'(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ (M=Cd or Hg) [24]. This vibrational mode splits into a doublet in $\text{Cd}(\text{pyrazine})\text{M}(\text{CN})_4 \cdot \text{C}_6\text{H}_6$ (M=Cd or Hg) [6] and $\text{M}(\text{NH}_3)_2\text{M}'(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ (M=Mn or Cd, M'=Cd or Hg) [22] and into a triplet in $\text{M}(\text{ethylenediamine})\text{M}'(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ (M=Mn or Cd, M'=Cd

or Hg) [25]. In the case of clathrates with triplet or doublet features, the splittings have been ascribed to crystal field effects (strong host-guest interactions) [25]. In the case of clathrates with a single band, because of the larger cavities due to the ligands, the host–guest interactions are expected not to be effective for splitting [24].

Based on the present data, it is not possible to determine the orientation of the benzene molecules in the host lattice in our clathrate compounds. As mentioned previously, the relative orientation of the N–H bonds of CHA with respect to the axis of the π cloud of benzene must be the one the most favourable for the hydrogen bonding [17].

The preceding discussion considered as a whole leads us the conclusion that the host lattice of our clathrates are similar to those of the other T_d -type clathrates.

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