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An Infrared Spectroscopic Study of Pyrazine- and 4,4′-bipyridyl-T_d-type Clathrates: Mn (pyrazine) $M(CN)_4$ benzene (M = Cd or Hg) and Mn (4,4′-bipyridyl) $M(CN)_4$. benzene (M = Zn, Cd or Hg)

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Abstract

The infrared spectra of the title compounds have been reported. The spectral data suggest that the host framework of these compounds are similar to those of the en-T_d-type clathrate compounds. There is good evidence for hydrogen bonding from ligand molecules to benzene molecules as a π to σ hydrogen bond.

Introduction

It has been shown that the host structures of the en-T_d-type clathrates provide thermally unstable radicals such as the cyclohexadienyl, $C_6H_7^{\cdot}$, radical with cavities surrounded by a chemically-inactive wall [1, 2]. These compounds are formulated as Cd $LM(CN)_4$.nG (abbr. Cd-L-M-G), where L is a bidentate ligand molecule, M is Cd or Hg and n is the number of G (guest) molecules depending on the bulkiness of the ligands. The host framework is formed from endless chains of -Cd-L-Cd- extending along the *a*- and *b*-axes alternately and the tetrahedral $M(CN)_4$ ions arranged between the consecutive crossing -Cd-L-Cd-L- chains with the N-ends bound to the Cd atoms [3–8]. This structure provides two kinds of cavities, α and β, for the guest molecules. The α cavity is a rectangular box similar to those in Hofmann-type hosts, while the β cavity is a twisted biprism, as has been demonstrated in previous papers [2–4, 7].

In our previous papers, we reported that the infrared and Raman spectral results suggest that the structure of Cd(pyrazine)$M(CN)_4$.Benzene (abbr. Cd-pyz-M-Bz) (M=Cd or Hg) [9] and Cd(4,4′-bipyridyl)$M(CN)_4$.2Benzene (abbr. Cd-bipy-M-2Bz) (M=Cd or Hg) [10] compounds are similar to those of the Td-type clathrates.

We have now replaced the metal atoms by new ones and prepared five new title compounds. In this study we report the infrared spectra of these clathrate compounds (Raman spectra of these beige compounds could not be obtained by using the 488 or 515 nm laser line).

Experimental

All chemicals used were reagent grade (Merck) and used without further purification.

The clathrate compounds were prepared in a N_2-atmosphere by adding slightly more than one millimole of pyrazine or 4,4′-bipyridyl solution in ethanol and one millimole of potassium tetracyanometallate solution in water saturated with benzene to one millimole of Mn(II) chloride solution in water, saturated with benzene. The beige precipitate was filtered, washed with water, ethanol and ether, successively, and stored in a desiccator containing benzene vapour.

The freshly prepared compounds were analyzed for C, H and N by a Leco CHN-600 Model analyzer with the results as follows (found %/calculated %):

Mn-pyz-Cd-Bz: C = 38.39/39.14, H = 2.29/2.35, N = 18.98/19.56,
Mn-pyz-Hg-Bz: C = 31.78/32.47, H = 2.00/1.95, N = 15.93/16.23,
Mn-bipy-Zn-Bz: C = 46.72/47.50, H = 2.88/2.79, N = 16.01/16.62,
Mn-bipy-Cd-Bz: C = 39.90/40.45, H = 2.44/2.38, N = 13.68/14.15,
Mn-bipy-Hg-Bz: C = 52.29/52.37, H = 3.18/3.07, N = 17.88/18.32.

These analytical results are often poor for samples obtainable only in powder form owing to partial decomposition. Such instability has been reported for the other T_d-type clathrates having guest species of low boiling points [12, 15]. The above results are in agreement with the following formulae: Mn-pyz-Cd-Bz, Mn-pyz-Hg-Bz, Mn-bipy-Zn-Bz, Mn-bipy-Cd-Bz and Mn-bipy-Hg-Bz.

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Table 1. The vibrational wavenumbers (cm^{-1}) of pyrazine in Mn-pyz-M-Bz (M = Cd or Hg) clathrates

Symmetry and assignment[a]		Pyrazine solution		Cd-pyz-Cd-Bz[c]		Cd-pyz-Hg-Bz[c]		Mn-pyz-Cd-Bz	Mn-pyz-Hg-Bz
		IR[a]	Ra[b]	IR	Ra	IR	Ra	IR	IR
16b;	B_{2u} γ_{ring}	418	–	448vs	no	448vs	no	448vs	448vs
6b;	B_{2g} δ_{ring}	–	701	no	699w	no	700w	no	no
4b;	B_{3g} γ_{ring}	–	756[d]	no	748vw	no	747vw	no	no
11;	B_{2u} γ(CH)	785	–	801vs	no	801vs	no	810vs	810vs
10a;	B_{1g} γ(CH)	–	919	no	914vw	no	913vw	no	no
5;	B_{3g} γ(CH)	–	983[d]	no	982wsh	no	982wsh	no	no
1;	A_g ν_{ring}	–	1011	no	1028vs	no	1028vs	no	no
12;	B_{1u} δ_{ring}	1019	–	1048vs	no	1048vs	no	1048vs	1048vs
15;	B_{3u} δ_{CH}	1061	–	1079m	no	1080m	no	1078s	1078s
18a;	B_{1u} δ_{CH}	1130	–	1128sp 1125sp	no	1128s	no	1128s	1128s
14;	B_{3u} γ_{ring}	1150	–	1158s	no	1158s	no	1155s	1155s
9a;	A_g δ(CH)	–	1231	no	1230m	no	1229m	no	no
3;	B_{2g} δ(CH)	–	1343	no	1352vw	no	1351vw	no	no
19b;	B_{3u} ν_{ring}	1412	–	1422s	no	1422s	no	1420s	1419s
19a;	B_{1u} ν_{ring}	1483	–	1490w	no	1490w	no	1479s	1479s
8b;	B_{2g} ν_{ring}	–	1524	no	1531w	no	1531w	no	no
8a;	A_g ν_{ring}	–	1574	no	1586w	no	1586w	no	no
13;	B_{1u} ν(CH)	3011	–	no	3034s	no	3034s	3064s	3064s
7b;	B_{2g} ν(CH)	–	3040	no	3053sh[e]	no	nm	no	no
2;	A_g ν(CH)	–	3054	no	3078s	no	nm	no	no
20b;	B_{1u} ν(CH)	3061	–	3119m	no	3110m	no	3100m	3100m

[a] Taken from ref. [24].
[b] Taken from ref. [20].
[c] Taken from ref. [9].
[d] Liquid phase value.
[e] Overlapped with benzene band, v = very, s = strong, m = medium, w = weak, sh = shoulder, sp = split, nm = not measured and no = not observed.

Infrared spectra of the compounds were recorded between 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 (without grinding) in nujol and hexachlorobutadiene between CsI windows and as KBr discs.

Results and discussion

The compounds studied show no major difference in the infrared spectra of the compounds with similar ligands (Figure 1). These similarities (with the exception of $Zn(CN)_4$ bands, see below) suggest that they also have similar structural features. These, in turn, suggest that the degree of the interactions of the benzene, ligand and $M(CN)_4$ species with their surroundings are almost the same for each clathrate. It will be most convenient to divide the vibrations into three groups arising from the $M(CN)_4$ units, from the ligand molecules and from the benzene moieties. The assignments of the spectral bands due to the $M(CN)_4$ benzene species are straightforward since these bands are persistent and picked out with ease [9–15].

Ligand vibrations

PYRAZINE: Evidence that the pyrazine molecule ($C_4H_4N_2$) has the centro symmetric and planar structure with D_{2h} symmetry in the vapour and solid phases has been provided by electron diffraction [16, 17] and X-ray diffraction [18, 19] studies, respectively. The assignments of the infrared and Raman spectra of pyrazine in the solid [20], liquid [21, 22] and vapour [23, 24] phases and in solution [20, 24] have been reported to be in accord with the D_{2h} symmetry. The vibrational spectral features of pyrazine in Hofmann-type $Cd(pyrazine)Ni(CN)_4.0.5C_6H_6$ [25] and Td-type $Cd(pyrazine)M(CN)_4.C_6H_6$ (M = Cd or Hg) clathrates [9] are also in accord with D_{2h} symmetry. In metal complexes in which both nitrogen atoms of pyrazine are coordinated to two identical metal atoms, the D_{2h} symmetry is preserved, but is removed in unidentate coordination [26, 27].

Table 1 tabulates the infrared wavenumbers of the compounds, together with the infrared and Raman wavenumbers of pyrazine in solution and Cd-pyz-Cd-Bz and Cd-pyz-Hg-Bz clathrates for comparison.

A glance at Table 1 shows that the pyrazine modes of the clathrate compounds exhibit coordination properties, that is, several modes of pyrazine have upward shifts in wavenumber in comparison with those of pyrazine in solution [9, 20, 24, 25]. The frequencies of the pyrazine molecules in

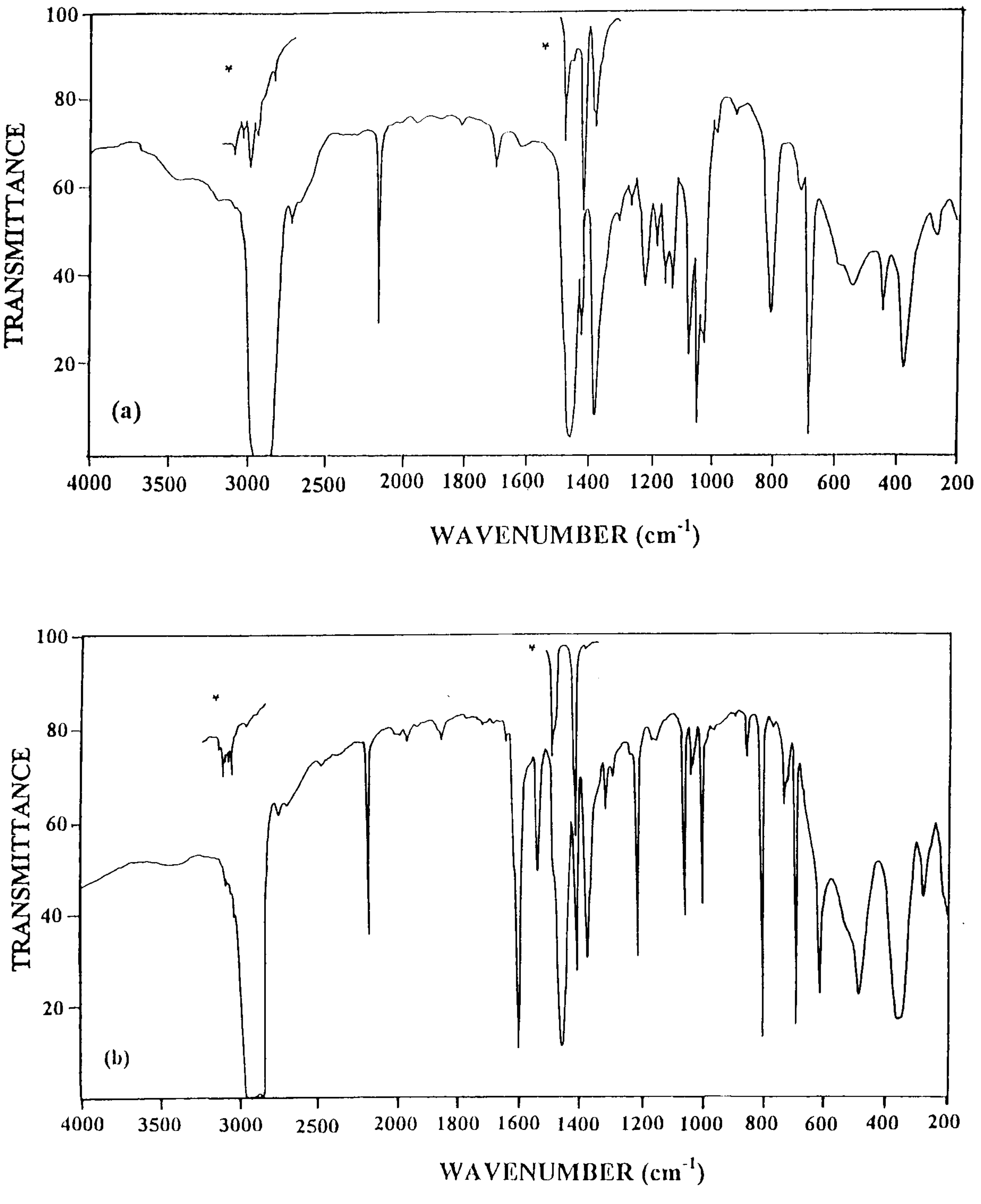

Figure 1. Infrared spectra of Mn-pyz-Cd-Bz; (a) and Mn-bipy-Cd-Bz; (b) clathrates in nujol (* in poly (chlortrifluorethylene)-oil).

the compounds studied are found to be very similar, indicating that the pyrazine frequency values are not affected by the slight changes in unit cell dimensions, if the metal M (here M = Mn), to which pyrazine is attached, is the same. Similar observations were made for the Cd-pyz-M-Bz (M = Cd or Hg) (M = Cd or Ni) clathrates [9]. In this context, it is noted that the wavenumbers of pyrazine in M(pyz)Ni(CN)$_4$.nC$_6$H$_6$ (M = Cd or Ni) clathrates are found to be greatly altered by changing the metal M from Cd to Ni, which was explained as the coupling of the internal modes of pyrazine with the M-N(pyrazine) vibrations [25]. The absence of such frequency alternations in our clathrates of the form M(pyz)M′(CN)$_4$.C$_6$H$_6$ (abbr. M-pyz-M′-Bz) implies that M is Mn and M′ is Cd or Hg; i.e., Mn is in the octahedral and M′ is in the tetrahedral environment as described above.

In the spectra of our compounds (Table 1), the absence of additional bands due to the infrared active bands expected for D_{2h} symmetry implies the bidentate coordination of pyrazine in the compounds presented.

Table 2. The vibrational wavenumbers (cm^{-1}) of 4,4′-bipyridyl in Mn-bipy-M-Bz (M = Zn, Cd or Hg) clathrates

Symmetry and assignment[a]		4,4′-bipyridyl		Cd-bipy-Cd-2Bz[b]	Cd-bipy-Hg-2Bz[b]	Mn-bipy-Zn-Bz	Mn-bipy-Cd-Bz	Mn-bipy-Hg-Bz
		Soild[a]	in CCl$_4$ [b]					
B_{3u}	1ν(CH)	3055	3062	3060w	3060w	3068w	3068w	3068w
	2ν(CH)	3047	–	3051w	3049w	3043w	3040w	3040w
	3ν_{ring}	1598	1583	1594vs	1594vs	l6OOvs	1598vs	1598vs
	4ν_{ring} + δ(CH)	1481	1481	1486m	1487m	1489m	1485m	1485m
	5δ_{ring}	1215	1212	1216vs	1216vs	1219vs	1215vs	1215vs
	6δ_{ring}	1044	1037	1064vs	1064vs	1064vs	1040m	1040m
	7ν_{ring}	994	987	1002vs	1002vs	1005vs	1001vs	1001vs
	8ν_{ring}	967	971	981w	981w	966w	950br	950br
	9ν_{ring}	615	604	617vs	617vs	628vs	620vs	620vs
B_{2u}	10ν(CH)	3078	–	3081m	3080m	3087m	3089vw	3089vw
	11ν(CH)	3029	3021	3031m	3030m	3033m	3020w	3020w
	12ν_{ring}	1532	1529	1532s	1534s	1531s	1532s	1529s
	13ν_{ring}	1413	1402	1410s	1410s	1412vs	1412vs	1410vs
	14δ(CH)	1324	1312	1315w	1316w	1317rn	1318m	1315m
	15δ(CH)	1223	–	1220sh	1220sh	1228sb	1232sh	1232sh
	16ν_{ring}	1074	1065	1075vw	1075vw	1064vs	1062vs	1062Vs
	17δ_{ring}	677	672	673w	670w	674w	670vw	670vw
	18 inter ring bend	–	–	no	no	no	no	no
B_{1u}	19γ(CH)	862	–	851m	850m	856w	852m	850m
	20γ(CH)	810	–	804vs	804vs	810vs	806vs	804vs
	21γ_{ring}	737	–	731s	729s	733m	730s	730s
	22γ_{ring}	507	501	490m	489m	501m	490m	490m
	23γ_{ring}	367	–	388m	387m	412m	395m	395m

[a] Taken from ref. [30].
[b] Taken from ref. [10]
v = very, s = strong, m = medium, w = weak, sh = shoulder and no = not observed.

4,4′ BIPYRIDYL: The 4,4′-bipyridyl molecule is non-planar in the vapour phase [28] and in the solid phase [29]. The dihedral angles between the two pyridine planes are ca. 35°. Nevertheless, the assignments based on the infrared and Raman spectra of the molecule in the solid phase and in the Hofmann-type M(4,4′-bipyridyl)Ni(CN)$_4$ (M = Ni or Cd) host complex and their dioxane, benzene, toluene, aniline and *N*,*N*′-dimethylaniline clathrates [30] and T_d-type Cd(4,4′-bipyridyl)M(CN)$_4$.2Benzene [10] clathrates have been reported as being in accord with the centrosymmetric and planar structure with D_{2h} symmetry. These spectral results imply that the dihedral angle between the two pyridine rings of ca. 35° is not effective to activate all of the vibrational modes with notable intensities in both infrared and Raman spectra. However, the criterion of the activity of the 4,4′-bipyridyl vibrations was used as evidence of the type of coordination viz. whether bidentate or unidentate and, on this basis, it was found that in metal complexes in which both nitrogen atoms are coordinated to identical metal atoms the vibrational exclusion principle is preserved [10, 30, 31] but is removed in unidentate coordination [31].

The assignments and the wavenumbers of the vibrational bands of 4,4′-bipyridyl in the infrared spectra of the compounds are listed in Table 2, together with the wavenumbers of 4,4′-bipyridyl in CCl$_4$ solution and in the T_d-type Cd(4,4′-bipyridyl)M(CN)$_4$.2Benzene (abbr. Cd-bipy-M-2Bz) (M = Cd or Hg) clathrates [10] on which the assignments are based. In assigning the vibrational bands D_{2h} symmetry is assumed for the 4,4′-bipyridyl molecule. Our assignment is in agreement with that of Sungur *et al.* [30].

The vibrational frequencies of the 4,4′-bipyridyl molecule in the compounds exhibit all the characteristics of a coordinated ligand, that is, several modes of 4,4′-bipyridyl with B_{3u} symmetry have upward shifts in wavenumber in comparison with those of 4,4′-bipyridyl in solution (Table 2), similar shifts are observed in the Hofmann-type complexes [30] and T_d-type clathrates [10] and explained by coupling of the internal vibration of the ligand with the M-N stretching vibration [10, 30]. These findings, and the absence of any bands additional to the infrared active bands expected on the basis of assumed D_{2h} symmetry implies the bidentate coordination of the 4,4′-bipyridyl ligand in our compounds.

M(CN)$_4$ group vibrations

In the T_d-type clathrates [9, 10, 12, 13, 15] and T_d-type host complexes [11, 14] studied previously, the metal atom M in M(CN)$_4$ is tetrahedrally surrounded by the carbon ends of four CN ions. Hence, it is reasonable to assume that the compounds studied here also possess tetrahedral M(CN)$_4$ (M = Zn, Cd or Hg) groups. In assigning the bands attributable to M(CN)$_4$ ions in the spectra, we refer to the work of Jones [33] who presented vibrational data for the salts $K_2M(CN)_4$ (M = Zn, Cd or Hg) in the solid state. The

Table 3. The vibrational wavenumbers (cm^{-1}) of the $M'(CN)_4$ group for the Mn-pyz-M-Bz (M = Cd or Hg) and Mn-bipy-M-Bz (M = Zn, Cd or Hg) clathrates*

Assignment[a]	$K_2Zn(CN)_4$ [a]	$K_2Cd(CN)_4$ [a]	$K_2Hg(CN)_4$ [a]	Cd-pyz-Cd-Bz[b]	Cd- pyz-Hg-Bz[b]	Mn-pyz-Cd-Bz	Mn-pyz-Hg-Bz	Cd-bipy-Cd-Bz[c]	Cd-bipy-Hg-Bz[c]	Mn-bipy-Zn-Bz	Mn-bipy-Cd-Bz	Mn-bipy-Zn-Bz
$\nu_1(CN)A_1$	(2157)	(2149)	(2149)	(2180vs)	(2180vs)	no	no	(2179vs)	(2179vs)	no	no	no
$\nu_5(CN)F_2$	2152	2145	2146	2176vs	2176vs	2170vs	2170vs	2165vs	2165vs	2173vs	2160vs	2160vs
Hot band	–	–	–	2164vw	2165Vw	no	no	2150w	2149w	no	no	no
$\nu_5(^{13}CN)$	–	–	–	no	no	2127vw	2132vw	no	no	2125vw	no	no
$\nu_2(MC)A_1$	(347)	(327)	(335)	no	no	no	no	(335vw)	(355w)			
$\nu_6[\nu(MC) + \delta(NCM)]F_2$	359	316	330	365vs	368vs	368vs	368vs	350vs	350vs	387vs	358vs	358vs
$\nu_7[\nu(MC) + \delta(NCM)]F_2$	315	250	235	no	no	268w	268w	270m	273m	331m	270w	270w

*Raman bands are in parentheses.

[a] Taken from ref. [33].

[b] Taken from ref. [9].

[b] Taken from ref. [10].

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

Table 4. The vibrational wavenumbers (cm^{-1}) of benzene in the Mn-pyz-M-Bz (M = Cd or Hg) and Mn-bipy-M-Bz (M = Zn, Cd or Hg) clathrates*

Assignment[a]	Liquid benzene[b]	Cd-pyz-Cd-Bz[c]	Cd-pyz-Hg-Bz[c]	Mn-pyz-Cd-Bz	Mn-pyz-Hg-Bz	Cd-bipy-Cd-Bz[d]	Cd-bipy-Hg-Bz[d]	Mn-bipy-Zn-Bz	Mn-bipy-Cd-Bz	Mn-bipy-Hg-Bz
$2\nu_8$	(3166)	(3163m)	nm	no	no	(3172m)	(3172m)	no	no	no
ν_{20}, E_{1u}	3073	3088s	3088s	3088w	3088w	no	no	3087m	3085m	3085m
$\nu_8 + \nu_{19}$	3075	no	no	3084w	3084w	3066m	3066m	3068m	3060m	3060m
ν_2, A_{1g}	(3062)	(3062m)	(3062m)	no	no	no	no	no	no	no
ν_{13}, B_{1u}	3048	3068m	3068m	3070vw	3070Vw	no	no	3033w	3030w	3030w
ν_7, E_{2g}	(3050)	(3053sh)	(3053sh)	no	no	no	no	no	no	no
$\nu_5 + \nu_{17}$, E_{1u}	1955	1951w	1951w	1965w	1965w	1980w	1980w	1973w	1967w	1967w
ν_8, E_{2g}	(1586)	(1586m)	(1586m)	no	no	(1587m)	(1587m)	no	no	no
$\nu_{10} + \nu_{17}$	1815	1822m	1822m	1820w	1820w	1836w	1834w	1830w	1827w	1827w
ν_{19}, E_{1u}	1479	1479w	1479w	1479s	1479s	1482w	1482w	1489m	1478m	1478m
ν_{14}, B_{2u}	1309	no	no	1303vw	1303vw	1315m	1315m	1317m	1294w	1294w
ν_9, E_{2g}	(1177)	(1179m)	(1177m)	no	no	(1178m)	(1178m)	no	no	no
ν_{15}, B_{2u}	1149	1147sh	1147sh	1150s	1150s	1149w	1149w	1155w	1150vw	1150vw
ν_{18}, E_{1u}	1036	1035m	1035m	1034s	1035s	1035s	1039s	1034m	1030m	1030m
ν_1, A_{1g}	(991)	(991vs)	(991vs)	no	no	(992m)	(992m)	no	no	no
ν_{10}, E_{1g},	(850)	(885vw)	(854vw)	no	no	(855w)	(855w)	no	no	no
ν_{11}, A_{2u}	670	685vs	685vs	686vs	686vs	695vs	695vs	685vs	684vs	684vs
		681vs	681vs	682vs	682vs	no	no	no	no	no

*Raman bands are in parentheses.
[a] Taken from ref. [40].
[b] IR bands from ref. [37], Raman bands from ref. [39].
[c] Taken from ref. [9].
[d] Taken from ref.[10].
v = very, s = strong, m = medium, w = weak, sh = shoulder, nm = not measured and no = not observed.

structural studies on these salts have shown that the K-CN distance is ca. 2.9Å in $K_2Zn(CN)_4$ [34], $K_2Cd(CN)_4$ [35] and $K_2Hg(CN)_4$ [36] while the Cd-NC distance is ca. 2.3Å in T_d-type host structures [6–8]. Hence, a similar distance might also be expected in our compounds. Therefore, the spectral data for $K_2M(CN)_4$ (M = Zn, Cd or Hg) can be used as references to account for the vibrational changes when the stiffer M-NC bonding takes place. The vibrational data for the $M(CN)_4$ groups in $K_2M(CN)_4$ (M = Zn, Cd or Hg) are given in Table 3, together with the spectral data for $Cd(CN)_4$ and $Hg(CN)_4$ units in some other clathrates for comparison with the assignments for the $M(CN)_4$ groups in our compounds. The assigned bands of the $M(CN)_4$ groups of the compounds appear to be much higher than those of $M(CN)_4$ in the $K_2M(CN)_4$ salts. Such upward shifts have been observed for T_d-type clathrates [9, 10, 12, 13] and T_d-type host complexes, [11, 14], in which both ends of the CN group are coordinated and explained as the mechanical coupling of the internal modes of $M'(CN)_4$ with the M-NC vibrations.

Benzene vibrations

The assignments and the wavenumbers of the vibrational bands arising from the enclathrated benzene observed in the spectra of the compounds are given in Table 4, along with the wavenumbers of benzene in the liquid phase [37] and in the Cd-pyz-Cd-Bz [9] and Cd-bipy-Cd-2Bz [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 is found to be shifted to higher frequency from that of liquid benzene. Similar shifts were observed for Hofmann-type [25,30] and T_d-type clathrates [9, 10, 12, 13] and explained by the presence of a weak hydrogen bond between the π electrons located above and below the benzene ring and the ligand molecules of the host lattices. Therefore, we may reasonably suggest that the frequency shifts in our compounds are due to the π electron donation from the benzene ring to the hydrogen atoms of the ligand molecules which have a more electrophilic character caused by the coordination.

Another feature of the out-of-plane CH bending vibration (A_{2u}) is that it appears as a very intense single band for Mn-bipy-M-Bz (M = Zn, Cd or Hg) and a doublet for Mn-pyz-M-Bz (M = Cd or Hg) (Table 4). This band has been observed as a singlet for Cd-bipy-M-2Bz (M = Cd or Hg) [10], a doublet in Cd-pyz-M-Bz (M = Cd or Hg) [9] and $M(NH_3)_2\ M'(CN)_4.2Bz$ (M = Mn or Cd, M′ = Cd or Hg) [12] and a triplet in M(ethylenediamine)$M'(CN)_4.2C_6H_6$ (M = Mn or Cd, M′ = Cd or Hg) [13]. In the case of clathrates with triplet or doublet features, the splittings have been ascribed to crystal field effects (strong host-guest interactions) [9, 10, 12, 13]. 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 [10].

Based on the present spectral data it is not possible to determine the orientation of the benzene molecules in the host lattice in our compounds. As in the Hofmann-type benzene and Hofmann-T_d-type benzene clathrates, the relative orientation of the H atoms of the ligand with respect to the axis of the π cloud of benzene must be the one most favorable for the hydrogen bonding [38].

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

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