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An Infrared and Raman Spectroscopic Study of pn-T_d-Type *dl*-Propylenediaminemetal(II) Tetracyanometallate(II) Benzene Clathrates: M(*dl*-pn)M′$(CN)_4$.nC_6H_6 (M = Mn, M′ = Zn, Cd or Hg; M = Cd, M′ = Cd or Hg; $1 \leq n \leq 1.5$)

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Abstract. IR spectra of Mn(*dl*-propylenediamine)M$(CN)_4$.nC_6H_6 (M = Zn, n = 1.25; M = Cd, n = 1.00 or M = Hg, n = 1.18), and IR and Raman spectra of Cd(*dl*-propylenediamine)M$(CN)_4$. 1.5C_6H_6 (M = Cd or Hg) are reported. The spectral data suggest that the former three compounds are similar in structure to the latter two pn-T_d-type clathrates.

Key words: clathrates, inclusion compounds, *dl*-propylenediamine, IR spectra, Raman spectra, benzene, manganese(II), zinc(II), cadmium(II), mercury(II).

1. Introduction

The powder X-ray difraction patterns of pn-T_d-type benzene clathrates Cd(pn)M$(CN)_4 \cdot 1.5C_6H_6$ (pn = *dl*-propylenediamine, M = Cd or Hg) (abbr. Cd-pn-M-Bz) [1] showed a close resemblance to those of the en-T_d-type clathrates Cd(en)M$(CN)_4 \cdot 2C_6H_6$ (en = ethylenediamine, M = Cd or Hg) (abbr. Cd-en-M-Bz) suggesting that the structure of the pn-type host is similar to that of the en-T_d-type host [2]. Such a host framework, say in Cd(en)Cd$(CN)_4 \cdot 2C_6H_6$ [3], is formed from infinite -Cd-en-Cd- chains extending along the *a*- and *b*-axes alternately and tetrahedral $Cd(CN)_4$ ions arranged between the consecutive crossing Cd-en-Cd-chains with N-ends bound to the Cd atoms. 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 illustrated in previous papers [4,5]. In the case of pn-T_d-type hosts, a pair of methyl groups are thought to occupy a cavity instead of a guest molecule similar to the Hofmann-pn-type [1]. We have prepared three similar new compounds of the form Mn(pn)M$(CN)_4 \cdot$ nC_6H_6 (M = Zn, n = 1.25; M = Cd, n = 1.00 or M = Hg, n =

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1.18) (abbr. Mn-pn-M). In the present investigation we study the IR spectra of Mn-pn-Zn, Mn-pn-Cd and Mn-pn-Hg (Raman spectra of these beige compounds could not be obtained by using a 488 or 515 nm laser line), and IR and Raman spectra of pn, Cd-pn-Cd-Bz and Cd-pn-Hg-Bz (for the latter two clathrate compounds, a T_d-type structure has been indicated by the powder X-ray diffraction studies [1]). It is noted that several unsuccessful attempts have been made to synthesize the host complexes of the clathrate compounds studied. This is presumably due to the high stabilities of their pn chelated complexes. Such stabilities have been reported for the en-chelated $Cd(en)Cd(CN)_4$ and $Cd(en)Hg(CN)_4$ compounds which are known as the residual hosts left after liberation of the guest benzene molecules from the respective Cd-en-Cd-Bz and Cd-en-Hg-Bz clathrates accompanied by the collapse of cavities [3]. The infrared spectra of the prepared host complexes M-pn-M′ (M = Mn, M′ = Cd or Hg; M = Cd, M′ = Cd or Hg) are also presented for comparison.

2. Experimental

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

The clathrates Mn-pn-M-Bz (M = Zn, Cd or Hg) were synthesized by adding one millimole of pn and one millimole of $K_2M(CN)_4$ solution in water to one millimole of $MnCl_2$ solution in water saturated with benzene. The beige powder precipitate was filtered, washed with water, ethanol and ether, successively, and kept in a desiccator containing moleculer sieve and saturated benzene vapour.

The clathrate compounds Cd-pn-Cd-Bz and Cd-pn-Hg-Bz were prepared by the methods already described in references [1]. The complexes $Mn(pn)\,M(CN)_4$ (M = Cd or Hg) and $Cd(pn)M(CN)_4$ (M = Cd or Hg) were prepared by the method used for Mn-pn-M-Bz (M = Zn, Cd or Hg) above in the absence of guest benzene.

The freshly prepared compounds were analyzed for C, H and N with the following results (found % / calculated %):

$Mn(C_3H_{10}N_2)Zn(CN)_4\cdot 1.25C_6H_6$: C = 43.51/43.96, H = 4.16/4.45, N = 20.03 /20.21.

$Mn(C_3H_{10}N_2)Cd(CN)_4\cdot 1.00C_6H_6$: C = 36.63/36.85, H = 4.77/3.80, N = 19.13 /19.83.

$Mn(C_3H_{10}N_2)Hg(CN)_4\cdot 1.18C_6H_6$: C = 32.33/32.15, H = 6.08/3.27, N = 16.18 /15.98.

$Cd(C_3H_{10}N_2)Cd(CN)_4\cdot 1.50C_6H_6$: C = 35.44/36.77, H = 3.55/3.67, N = 15.70 /16.20.

$Cd(C_3H_{10}N_2)Hg(CN)_4\cdot 1.50C_6H_6$:C = 32.15/31.66, H = 4.34/3.15, N = 13.65 /13.79.

$Cd(C_3H_{10}N_2)Cd(CN)_4$: C = 20.97/20.86, H = 2.32/2.50, N = 19.95 /20.85.

$Cd(C_3H_{10}N_2)Hg(CN)_4$: C = 17.50/17.11, H = 1.98/2.05, N = 17.75 /17.10.

$Mn(C_3H_{10}N_2)Cd(CN)_4$: C = 23.99/24.33, H = 3.02/2.91, N = 24.72 /24.32.

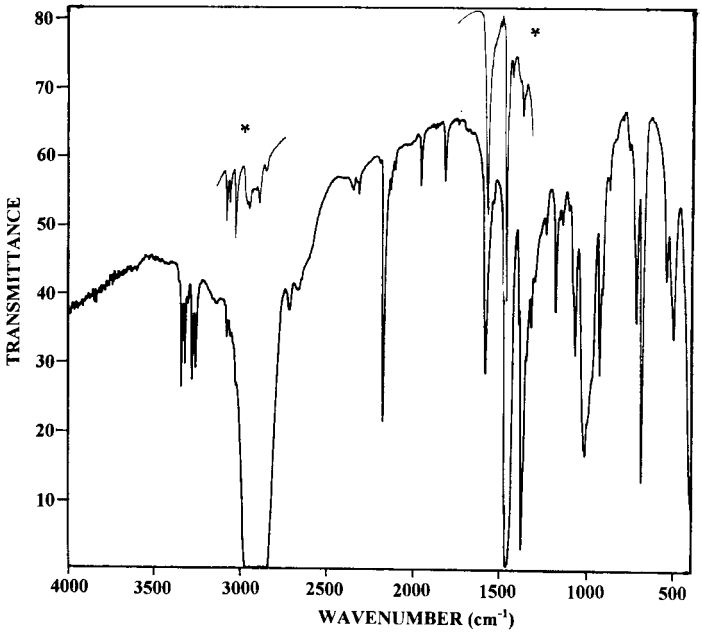

Figure 1. The infrared spectrum of the Mn-pn-Zn-Bz clathrate in nujol (* in hexachlorobutadiene).

$Mn(C_3H_{10}N_2)Hg(CN)_4$: C = 19.04/19.38, H = 2.41/2.32, N = 19.68 /19.37.

The analytical results are often poor for the samples obtainable only in powder form owing to partial decomposition. Such instability has been reported for the other T_d-type clathrates having as guest species low boiling point liquids [6,7]. These results suggest that the powder compounds with M = Mn orginated from the expected compound with n = 1.5.

IR spectra of the compounds were recorded in the range of 4000 to 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 hexachlorobutadiene between CsI plates (Figure 1). Raman spectra of the Cd-pn-Cd-Bz and Cd-pn-Hg-Bz clathrate compounds (in powder form) in a home-made spinning cell were excited using the 514.5 nm line of a Spectra-Physics Model 2016-4S argon-ion laser and recorded on a Jobin-Yvon U1000 spectrometer which was calibrated against the laser plasma emission lines.

3. Results and Discussion

The spectral features of the clathrate compounds with the same metal M 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 clathrate compounds with different crystal symmetry possibilities are not effec-

tive. The same is true for the host complexes. Owing to the lack of structural data, the assignment was made by treating the propylenediamine, the benzene molecules and the $M(CN)_4$ ions as isolated units. The wavenumbers and assignment of the observed bands in the infrared and Raman spectra of the compounds studied are given in Tables I–III for ligand pn, $M(CN)_4$ groups and guest benzene molecules, respectively, together with some pertinent spectral data for comparison. It should be noted that in the Raman spectra of the compounds with M = Cd, we could only dedect the $\nu_1(A_1)$ band of the $M'(CN)_4$ group (Table II) and the $\nu_1(A_1)$ band of the guest benzene molecule (Table III). This is due to the occurrence of fluorescence of high intensity and the relatively low scattering cross-section of the pn molecule.

3.1. PROPYLENDIAMINE VIBRATIONS

Up to the time of writing, there have been no reports concerning the vibrational spectral data for the pn molecule. Owing to the low symmetry of the pn molecule (C_1), the assignments of the pn vibrational bands in the spectra were made in terms of characteristic group frequencies.

The tentative assignments of the fundamental bands of pn observed in the spectra of the compounds under study are mainly based on the assignments of the vibrational bands of liquid ethylenediamine [8] and the $Cd(en)Cd(CN)_4 \cdot 2Bz$ clathrates [7] (Table I). For the purposes of comparison and discussion, Table I also includes some spectral data for pn in solution in CCl_4.

On comparing the spectra of the clathrates with M = Cd to those of the clathrates with M = Mn, the absence of the expected splittings due to the partial liberation of the guest molecules in the spectra of the clathrates with M = Mn suggest that the magnitudes of the splittings are too small to permit resolution.

Infrared spectral data for pn in the clathrate compounds would be expected to be consistent with all the vibrational features of a coordinated ligand, that is, on coordination, the N—H and N—C stretching frequencies should decrease, while the C—H and C—C frequencies should increase due to the consecutive inductive effects [9], in other words, on coordination N—H and N—C bonds should become weaker and C—H and C—C bonds become stronger. But in our case, this expectation is not fully realized and a nonsystemmatic frequency alteration has been observed for the $\nu(NH_2)$ stretching vibrations (Table I). This ambiguity was also observed in the spectra of en-T_d-type [7] and tn-T_d-type [10] benzene clathrates.

As expected, two bands are observed in the N—H stretching region, an antisymmetric NH stretch and a symmetric NH stretch [7,10]. The absence of splitting of these sharp bands imply the bidentate coordination of the ligand pn molecule in the clathrates.

Based on the present spectral data, it is not possible to determine the conformation of the pn molecules in our clathrate compounds.

On comparing the infrared bands attributable to the pn in clathrates with those of host complexes (Table I), it is seen that they are substantialy different in band

Table I. The vibrational wavenumbers (cm^{-1}) of propylenediamine in the M-pn-M′-Bz (M = Mn or Cd, M′ = Zn, Cd or Hg) clathrates and related compounds

Assignment[a]	liquid en[a]	pn in CCl_4	Cd-en-Cd-2Bz[b]	Cd-pn-Cd-Bz	Cd-pn-Hg-Bz	Mn-pn-Zn-Bz	Mn-pn-Cd-Bz	Mn-pn-Hg-Bz	Cd-pn-Cd	Cd-pn-Hg	Mn-pn-Cd	Mn-pn-Hg
$\nu(NH_2)$	3349 vs	3361 s	3316 m	3354 s	3352 s	3346 w	3348 w	3350 m	3344 vs	3344 s	3340 s	3342 s
$\nu(NH_2)$		3292 s	no	3323 m	3321 m	3317 m	3317 m	3319 m	3296 s	3296 m	3296 m	3298 m
$\nu(NH_2)$	3279 vs	3272 s	3283 vs	3292 s	3290 s	3286 w	3286 w	3288 w	3288 s	3288 m	3284 m	3286 m
$\nu(NH_2)$	3189 ms	3182 s	no	3269 m	3267 m	3267 m	3265 m	3265 m	no	no	no	no
$\nu(CH_3)$		2960 vs	2974 w	2951 m	2951 m	2958 m	2954 m	2954 m	2951 m	2954 m	2954 m	2949 m
$\nu(CH_2)$	2922 vs	2929 s	2943 m	2931 vw	2931 vw	2918 w	2918 w	2918 w	2943 w	2944 vw	2944 vw	2943 w
$\nu(CH_2)$	2853 vs	2870 m	2881 w	2881 m	2881 m	2894 m	2898 m	2892 m	2895 m	2893 m	2894 m	2891 m
$\nu(CH)$		2853 w	no	2852 w	2854 w	2846 w	2850 w	2848 w	2844 w	2844 w	2848 w	2854 w
$\delta(NH_2)$	1595 vs	1595 vs	1590 s	1587 s	1587 s	1581 s	1581 s	1581 s	1608 s	1604 m	1606 m	1608 m
$\delta(NH_2)$		no	1574 vs	1576 sh	1578 sh	1571 sh	1572 sh	1572 sh	1585 m	1583 w	1581 w	1581 w
$\delta(CH_2)$	1458 mw	1456 m	1458 m	1462 w	1462 w	1465 w	1462 w	1460 w	1466 w	1466 w	1462 w	1463 w
$\delta(CH_3)$		1433 vw	no	1433 vw	1436 vw	1437 vw	1436 vw	1437 vw	1433 m	1429 m	1429 m	1429 m
$\delta(CH_3)$		1377 m	no	1396 w	1394 w	1398 w	1396 vw	1396 w	1404 m	1402 w	1404 w	1404 w
$\omega(CH_2),\delta(CH)$	1356 mw	1350 w	1383 w	1352 w	1352 w	1352 w	1352 vw	1352 w	1359 w	1350 w,sh	1351 w,sh	1352 w,sh
$t(NH_2)$	1254 vw	1252 vw	no	1246 w	1248 w	1250 w	1247 w	1248 w	1278 m	1279 m	1278 w	1278 w
$t(NH_2)$		no	no	no	no	no	no	no	1209 w,sh	1234 w	1238 vw	1242 vw
$\rho(CH_3)$		1144 w	no	1149 vw	1149 vw	1149 vw	1147 w	1147 vw	1153 w	1153 w	1153 vw	1153 vw
ν(Skeletal)	1096 m	1093 s	1072 vs	1110 mw	1117 mw	1118 w	1118 w	1118w	1120 s	1120 s	1124 s	1124 s
ν(Skeletal)	1054 mw	1066 w	no	1070 m	1072 m	1080 s	1078 s	1076 s	1076 w	1074 w	1078vw	1080 vw
ν(Skeletal)	991 sh	1012 vw	no	1016 m	1018 m	1020 s	1018 s	1018 s	1028 s	1030 s	1034 m	1032 m
ν(Skeletal)		982 m,sh	991 vs	995 m	989 m	997 s	995 s	997 s	983 vs	985 vs	985 vs	987 vs
$\omega(NH_2)$	900 vs	934 sh	no	930 m	930 m	935 m	931 s	930 s	939 w	937 w	893 s	893 s
$\rho(CH_2)+\omega(NH_2)$	830 m	nm	769 vw	878 vw	879 vw	883 vw	881 w	879 m	891 s	893 s	874 m	874 m
na		nm	no	775 vw	773 vw	771 vw	775 w	773 w	771 vw	771 vw	769 vw	771 vw
na		619 vw	no	594 vvw	596 vvw	620 vw	617 vw	617 vw	no	no	617 m,sh	617 m,sh
na		no	no	538 mw	538 w	555 w	551 w	550 w	571 m	571 m	571 m	571 m
δ((Skeletal)	513 mw	509 vw	502 s	506 w	508 m	509 m	503 m	501m	509 m	509 m	509 m	505 m
δ((Skeletal)	475 w	472 vw	no	440 vw	440 vw	445 vw	442 vw	442 vw	455 m	455 m	457 w	449 w

[a] Taken from ref. [8]. [b] Taken from ref. [7]. v = very, s = strong, m = medium, w = weak, sh = shoulder, no = not observed, nm = not measured, na = not assigned.

Table II. The vibrational wavenumbers (cm^{-1}) of the $M'(CN)_4$ group for the M-pn-M′-Bz clathrates*

Assignment	$K_2Zn(CN)_4$[a]	$K_2Cd(CN)_4$[a]	$K_2Hg(CN)_4$[a]	Cd-en-Cd-Bz[b]	Cd-en-Hg-Bz[b]	Cd-pn-Cd-Bz	Cd-pn-Hg-Bz
$\nu_1(CN)A_1$	(2157)	(2149)	(2149)	(2170 vs)	(2175 vs)	(2171 s)	(2171 s)
$\nu_5(CN)F_2$	2152	2145	2146	2167 vs (2163 sh)	2169 vs (2168 sh)	2166 vs (2167 m)	2166 vs (2167 m)
Hot band	–	–	–	no	no	2133vw	2129vw
$\nu_2(MC)A_1$	(347)	(327)	(335)	no	no	no	no
$\nu_6[\nu(MC)+\delta(NCM)]F_2$	359	316	330	354 s	355 s	363 s	350 s
$\nu_7[\nu(MC)+\delta(NCM)]F_2$	315	250	235	269 w	270 m	253 w	253 w
Assignment	Mn-pn-Zn-Bz	Mn-pn-Cd-Bz	Mn-pn-Hg-Bz	Cd-pn-Cd	Cd-pn-Hg	Mn-pn-Cd	Mn-pn-Hg
$\nu_1(CN)A_1$	no	no	no	(2169 vs)	(2165 vs)	no	no
$\nu_5(CN)F_2$	2173 vs	2171 vs	2170 vs	2164 vs	2160 vs	2156 vs	2160 vs
Hot band	2150 vw	2121 vw	2120 vw	2113 vw	2118 vw	2113 vw	2116 vw
$\nu_2(MC)A_1$	no	no	no	no	no	no	no
$\nu_6[\nu(MC)+\delta(NCM)]F_2$	375 s	352 s	356 s	350 s	350 s	350 s	350 s
$\nu_7[\nu(MC)+\delta(NCM)]F_2$	325 w	268 w	265 w	262 w	262 w	264 w	264 w

*Raman bands are in parentheses. [a] Taken from Ref. [11]. [b] Taken from Ref. [7]. v = very, s = strong, w = weak, m = medium, sh = shoulder, no = not observed.

Table III. The vibrational wavenumbers (cm^{-1}) of benzene in the M-pn-M′-Bz clathrates*

Assignment[a]	Liquid Benzene[b]	Cd-en-Cd-Bz[c]	Cd-en-Hg-Bz[c]	Cd-pn-Cd-Bz	Cd-pn-Hg-Bz	Mn-pn-Zn-Bz	Mn-pn-Cd-Bz	Mn-pn-Hg-Bz
ν_8	(3166)	no	no	no	no	no	no	no
ν_{20} E_{1u}	3073	3085m	3086m	3086m	3086m	3087m	3086m	3086m
$\nu_8+\nu_{19}$	3075	3066m	3064m	3065w	3065w	3070w	3066m	3066w
ν_2 A_{1g}	(3062)	3062vw	3060vw	3065w	3065w	no	no	no
		(3060s)	(3059s)	no	no	no	no	no
ν_{13} B_{1u}	3048	3028s	3032s	3032m	3031m	3035m	3033m	3033m
ν_7 E_{2g}	(3050)	3042vw	3045vw	no	no	no	no	no
		(3044s)	(3044s)	no	no	no	no	no
$\nu_5+\nu_{17}$ E_{1u}	1955	1960w	1964w	1967w	1969w	1967w	1963w	1963w
ν_8 E_{2g}	(1586)	(1584m)	(1585m)	no	no	no	no	no
$\nu_{10}+\nu_{17}$	1815	1818w	1820w	1822 w	1824w	1824 w	1820w	1817w
ν_{19} E_{1u}	1479	1477s	1479s	1477s	1477s	1479s	1477s	1477s
ν_{14} B_{2u}	1309	1309w	1310w	1306w	1308w	1309w	1307w	1309w
ν_9 E_{2g}	(1177)	1176vw	1169vw	1184w	1184w	1188w	1186w	1186w
		(1176w)	(1175w)	no	no	no	no	no
ν_{15} B_{2u}	1149	1147vw	1146vw	1149vw	1149vw	1149vw	1147vw	1147vw
ν_{18} E_{1u}	1036	1033m	1034m	1032s	1034s	1037s	1037s	1034s
ν_1 A_{1g}	(991)	(992vs)	(992vs)	(992vs)	(992vs)	no	no	no
ν_{10} E_{1g}	(850)	853vw	849vw	no	no	no	no	no
ν_{11} A_{2u}	670	695sh	694s	694s	694s,sh	690s,sh	692s,sh	690s,sh
		683vs	688vs	683vs	684vs	684vs	683vs	681vs
		676sh	679sh	no	no	no	no	no
ν_6 E_{2g}		604vw	601vw	no	no	no	no	no
	(607)	(605vw)	(606vw)	no	no	no	no	no

* Raman bands are in parentheses. [a] Taken from ref. [24]. [b] IR bands from ref. [19], Raman bands from ref. [22]. [c] Taken from ref. [7]. v = very, s = strong, w = weak, m = medium, sh = shoulder, no = not observed.

patterns and in frequencies suggesting that the conformation of pn molecules in clathrates are substantially different from those in host complexes. As mentioned above (Section 1), these differences may possibly be due to the chelating behaviour of the pn ligand in the host complexes, since the chelating arrangments have been shown in $Cd(en)Cd(CN)_4$ and $Cd(en)Hg(CN)_4$ complexes [3].

3.2. $M'(CN)_4$ GROUP VIBRATIONS

In assigning the bands attributable to $M'(CN)_4$ (M = Zn, Cd or Hg) ions in the spectra of our compounds, we refer to the work of Jones [11] who presented vibrational data for the salts $K_2M(CN)_4$ (M = Zn, Cd or Hg) in the solid phase and assigned the infrared and Raman active fundamental vibrations of the $M(CN)_4$ ion on the basis of T_d symmetry. The structural studies on these salts have shown that the K—NC distances are ca. 2.9 Å in $K_2Zn(CN)_4$ [12], $K_2Cd(CN)_4$ [13] and $K_2Hg(CN)_4$ [14], while the Cd—NC distances are ca. 2.3 Å in T_d-type host frameworks [5]. Thus, they can be used as references to account for the vibrational changes when the stiffer Cd—NC bonding takes place. The vibrational data for $M'(CN)_4$ groups in the clathrate compounds under study are given in Table II, together with the vibrational wavenumbers of $K_2Zn(CN)_4$, $K_2Cd(CN)_4$ and $K_2Hg(CN)_4$ [11]. The assigned wavenumbers for the $M'(CN)_4$ groups in the compounds studied appear to be much higher than those for $M(CN)_4$ groups in $K_2M(CN)_4$ (M = Zn, Cd or Hg) (Table II). Such frequency shifts have been observed for other T_d-type clathrates [7,10] and T_d-type host complexes [15,16], 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 = Zn, Cd or Hg) with the M—NC vibrations [7,10,15,16]. It follows that the N-ends of the $M'(CN)_4$ groups are also bound to a M atom in our clathrate compounds.

3.3. BENZENE VIBRATIONS

Vibrational spectral data for benzene in a number of T_d-type clathrates have been presented [7,10,17,18]. The assigments and the frequencies of the vibrational bands of benzene observed in the infrared and Raman spectra of the compounds are given in Table III, along with the wavenumbers of benzene in the liquid phase [19] and in the Cd-en-Cd-Bz clathrate [7] for comparison. The most structurally informative spectral features are the following.

Most of the vibrational bands of the isolated benzene molecules are observed in the infrared spectra of the clathrates (Table III), suggesting that the selection rules for the benzene molecule under its intrinsic symmetry (D_{6h}) are lost. This is possibly due to the lower site symmetry of the benzene molecules in the clathrates.

The CH out-of-plane mode (A_{2u}) in the infrared spectra of the clathrates appears as a singlet for $Cd(4,4'\text{-bipyridyl})M(CN)_4 \cdot 2C_6H_6$ (M = Cd or Hg) [18], a doublet for the present compounds (Table III) and for $Cd(pyrazine)\ M(CN)_4 \cdot C_6H_6$ (M = Cd

or Hg) [17] and for $M(tn)Zn(CN)_4 \cdot 2C_6H_6$ (M = Mn or Zn) [20], and a triplet for $M(en)M'(CN)_4 \cdot 2C_6H_6$ (M = Mn or Cd, M′ = Cd or Hg) [7]. In the case of clathrates with triplet or doublet features, splittings have been ascribed to crystal field effects (strong host-guest interactions) [7]. 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 [18].

Another feature of the $\nu_{11}(A_{2u})$ mode is that it is found to be shifted to higher frequency (Table III) from that of liquid benzene (670 cm^{-1}) [19]. Similar shifts were observed for Hofmann-type [21,22] and T_d-type [7,10,17–20,23] clathrates. This upward shift may be due to a weak hydrogen bond between the π electrons located above and below the plane of the benzene ring and the pn ligand molecules of the host framework, as has been suggested for other clathrates [7,10,17,18,20–23]. Therefore, we reasonably suggest that the frequency shifts in our clathrates are due to the π electron donation from the benzene ring to the hydrogen atoms of the pn which have a more electrophilic character caused by the bidentate coordination.

The preceeding discussion considered as a whole leads us to the conclusion that the host lattice of the clathrates Mn-pn-Zn-Bz, Mn-pn-Cd-Bz and Mn-pn-Hg-Bz are similar to those of the pn-T_d-type, Cd-pn-Cd-Bz and Cd-pn-Hg-Bz clathrate compounds.

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