

Vibrational Spectroscopic Studies on the tn-Td-Type $\text{Mn}(\text{tn})\text{Zn}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ and the Chelated tn-Td-Type $\text{Zn}(\text{tn})\text{Zn}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ Clathrates

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Abstract. IR spectra of $\text{Mn}(\text{trimethylenediamine})\text{Zn}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ and IR and Raman spectra of $\text{Zn}(\text{trimethylenediamine})\text{Zn}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ are reported. The spectral data suggest that the host frameworks of these compounds are similar to those of the tn-Td-type $\text{Cd}(\text{trimethylenediamine})\text{M}(\text{CN})_4 \cdot 2\text{benzene}$ ($\text{M} = \text{Cd}$ or Hg) and the chelated pn-Td-type $\text{Cd}(\text{propylenediamine})\text{Cd}(\text{CN})_4 \cdot 1,2\text{-dichloroethane}$ clathrates, respectively.

Key words: Clathrates, inclusion compounds, trimethylenediamine, tetracyanozincate, benzene, IR spectra, Raman spectra.

1. Introduction

We are currently involved in the preparation and spectroscopic structural description of the Td-type clathrate compounds which are derived from the original benzene clathrates $\text{Cd}(\text{ethylenediamine})\text{M}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ ($\text{M} = \text{Cd}$ or Hg) [1] by appropriate replacements of the host moieties [2–6]. In our previous study [6], vibrational spectral data of $\text{Mn}(\text{tn})\text{M}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ (tn = trimethylenediamine, $\text{M} = \text{Cd}$ or Hg) (abbr. Mn-tn-M-Bz) have been structurally correlated with those of Td-type clathrates $\text{Cd}(\text{tn})\text{M}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ ($\text{M} = \text{Cd}$ or Hg) (abbr. Cd-tn-M-Bz) [7]. In the host frameworks of these compounds, the M atom is tetrahedrally coordinated to the carbon atoms of the four cyanide groups, while the Cd (or Mn) atom is octahedrally surrounded by six nitrogen atoms, two are from two different tn molecules attached to the Cd (or Mn) 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 $\text{Cd}(\text{tn})_2$ moieties to form a three-dimensional network. This structure provides two kinds of cavities, α and β , for the guest benzene molecules [8–10]. The former cavity approximates to a rectangular box and the latter to a biprismatic cage, as shown in Figure 1 [9].

The host framework described above is not unique for the given chemical formula above. A number of papers have suggested that similar compositions never support similar structures for the cyanometallate inclusion and complex systems [10–

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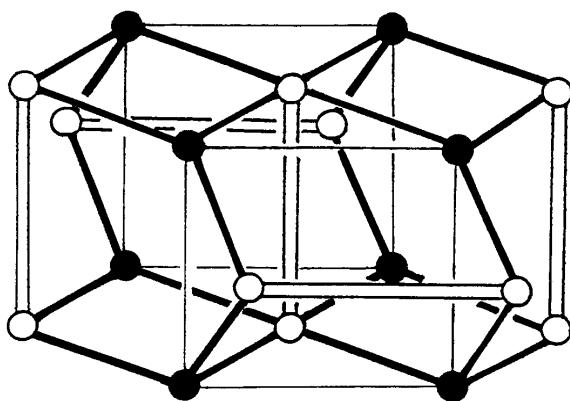


Figure 1. Structural model of the tn-Td-type host, $M(\text{tn})M'(\text{CN})_4$, open circle, 6-coordinate M; solid circle, tetragonal M' ; open column, a tn ligand; thick line, CN bridge; and thin line, edge of cavity.

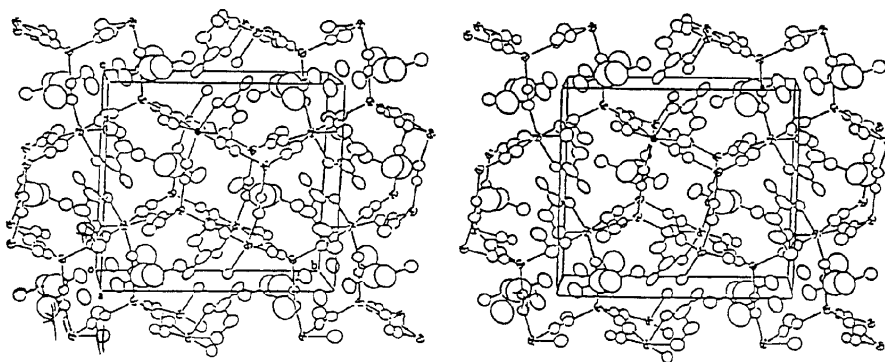


Figure 2. A stereoview of the unit cell of Cd-pn-Cd-DCE along the a -axis. Six coordinate Cd is shown as a solid circle.

20]. Of these compounds, the most relevant one for the purpose of discussion below is the 1,2-dichloroethane clathrate, $\text{Cd}(\text{propylenediamine})\text{Cd}(\text{CN})_4 \cdot \text{ClCH}_2\text{CH}_2\text{Cl}$ (abbr. Cd-pn-Cd-DCE) [18]. The three-dimensional host of this compound is comprised of the cyanide linkages between the pn-chelated octahedral Cd and the tetrahedral Cd of tetracyanocadmate. A pair of the guest 1,2-dichloroethane molecules are accommodated in the cage-like cavity cornered with fourteen Cd atoms, eight of them being the pn-chelated octahedral Cd atoms. At both sides of the cavity the corners are not linked with cyanide groups but each of the chelated pn ligands plays the role of a wall separating cavities one from the other (Figure 2) [18]. The present authors wish to name the host framework of this compound 'chelated pn-Td-type'.

The clathrate compounds possessing the above types of host structures reported to date have only been confined to those with a Mn or Cd metal atom in the octahe-

dral environment and Cd or Hg in the tetrahedral group [1–10]. We have now prepared two new compounds of the form $\text{Mn}(\text{trimethylenediamine})\text{Zn}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ (abbr. Mn-tn-Zn-Bz) and $\text{Zn}(\text{trimethylenediamine})\text{Zn}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ (abbr. Zn-tn-Zn-Bz). In this study we report the IR spectra of Mn-tn-Zn-Bz and IR and Raman spectra of Zn-tn-Zn-Bz (Raman spectra of the former beige compound could not be obtained by using the 488 nm or 415 nm laser line). The spectral data are structurally correlated with those of Mn-tn-Cd-Bz, Mn-tn-Hg-Bz, Cd-tn-Cd-Bz and Cd-tn-Hg-Bz. For the latter two clathrates, Td-type structures have been indicated by the powder X-ray diffraction patterns [7]. It should be noted that several unsuccessful attempts have been made to synthesize similar clathrates with Fe, Co or Cu in the octahedral arrangement.

2. Experimental

2.1. PREPARATIONS

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

The preparation of the clathrate Mn-tn-Zn-Bz (or Zn-tn-Zn-Bz) was similar to that of Mn-tn-M-Bz ($M = \text{Cd}$ or Hg) [6]: a solution composed of 1 millimole of $\text{K}_2\text{Zn}(\text{CN})_4$ and 1 millimole of tn in water saturated with benzene was added to a solution of MnCl_2 (or ZnCl_2) in water. The precipitate (very fine powder) was filtered, washed with water, ethanol and ether, successively, and kept in a desiccator containing saturated benzene vapour.

The freshly prepared samples were analyzed for C, H and N with the following results (found %, calculated %): $\text{Mn}(\text{C}_3\text{H}_{10}\text{N}_2)\text{Zn}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$: C = 48.22/50.18, H = 4.67/4.88, N = 18.70/18.48; $\text{Zn}(\text{C}_3\text{H}_{10}\text{N}_2)\text{Zn}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$: C = 47.04/49.05, H = 4.52/4.77, N = 18.11/18.07.

These analytical results are poor for the samples obtainable in powder form because of partial decomposition (the results indicate ca. 1.8 C_6H_6). Such instabilities have been reported for some Td-type clathrates having low boiling point guest molecules [6, 7].

2.2. SPECTRA

IR spectra of the freshly prepared compounds were recorded between 4000 cm^{-1} and 200 cm^{-1} on Perkin Elmer 1330 and Mattson 1000 FTIR spectrometers, which were calibrated using polystyrene and indene. The samples were prepared as mulls in Nujol and hexachlorobutadiene in a CsI cell and as KBr discs. Raman spectra of the Zn-Zn-tn-Bz clathrate (in powder form) in a home-made spinning cell or in a slurry in a circulating loop using a peristaltic pump were excited using the 514.5 nm line of a Spectra-Physics Model 2016-4S argon ion laser and recorded on a Jobin-Yvon 1000 spectrometer which was calibrated against the laser plasma emission lines.

3. Results and Discussion

The compounds under study show no serious difference between the infrared spectra recorded in Nujol (or hexachlorobutadiene) mulls and KBr pellets. Because of the lack of structural data, the assignment was made by treating the tn, $\text{Zn}(\text{CN})_4$ and bz moieties as isolated units.

3.1. TRIMETHYLENEDIAMINE VIBRATIONS

Few studies have been reported on the vibrational spectra of trimethylenediamine and coordinated trimethylenediamine in metal complexes. Of these, three reports are relevant to our purpose. Segal and Eggerton [21] presented infrared spectral data for α, ω -diamines from ethylene- to octamethylenediamine in solution in CCl_4 and in a KBr pellet in the frequency range of $4500\text{--}650\text{ cm}^{-1}$. Fleming and Shepherd [22] presented infrared spectral data for the chelate complex $\text{Cu}(\text{tn})_2(\text{PF}_5)_2$ in the frequency region of $4000\text{--}250\text{ cm}^{-1}$. They made the assignment for the coordinated ligand in the *cis*-conformation in terms of group frequencies and their assignment is supported by normal coordinate analysis. In our previous paper [6] we presented the vibrational spectral data for tn in solution in CCl_4 and in Td-type clathrate compounds, $\text{M-tn-M}'\text{-Bz}$ ($\text{M} = \text{Cd}$ or Mn , $\text{M}' = \text{Cd}$ or Hg).

The assignments and the wavenumbers of the fundamental bands of tn observed in the spectra of the compounds studied are listed in Table I. For the purposes of comparison and discussion, Table I also includes some spectral data for tn in solution in CCl_4 , $\text{M-tn-M}'\text{-bz}$ ($\text{M} = \text{Mn}$ or Cd , $\text{M}' = \text{Cd}$ or Hg) clathrates [6], and the $\text{Cu}(\text{tn})_2(\text{PF}_6)_2$ [22] complex. The infrared frequencies of our tn solution in CCl_4 are in good agreement with those reported previously [6, 21]. It should be noted that our previous report on the $\text{M-tn-M}'\text{-Bz}$ clathrates contained a few errors in the assignments of tn bands [6]. These have been reassigned (Table I). It should be noted that in Table I two assignments were made for each CH_2 vibration due to their being in two different environments.

The spectral appearance of the tn bands in the infrared spectrum of the Mn-tn-Zn-Bz clathrate is substantially different from that of Zn-tn-Zn-Bz (Table I). Some bands with considerable intensities (e.g., 1463, 1294, 1109, 1012 and 652 cm^{-1}) in the infrared spectrum of Zn-tn-Zn-Bz are absent or appear with weak or very weak intensities in the other. This spectral dissimilarity implies two different spatial arrangements of the tn molecule as a ligand. The bridging *gauche* conformation for the tn molecule in Cd-tn-Cd-Bz and in Cd-tn-Hg-Bz clathrates has been suggested by powder X-ray diffraction studies [7]. A glance at Table I shows that each of the fundamental bands in the infrared spectra of Cd-tn-Cd-Bz and Cd-tn-Hg-Bz is faithfully reproduced with only minor shifts in the spectrum of the Mn-tn-Zn-Bz compound. This striking correspondence suggests a bridging *gauche* conformation for the tn molecule in the Mn-tn-Zn-Bz clathrate compound.

Table I. The vibrational wavenumber (cm^{-1}) of trimethylenediamine in the M-tn-Zn-Bz clathrates.

Assignment ^a	tn in CCl_4	Cd-tn-Cd-Bz ^a	Cd-tn-Hg-Bz ^a	Mn-tn-Cd-Bz ^a	Mn-tn-Hg-Bz ^a	Cu(tn) ₂ (PF ₆) ₂ ^b	Mn-tn-Zn-Bz	Zn-tn-Zn-Bz
ν_a (NH ₂)	3365vs	3352s	3348s	3350s	3343s	3300–3200s	3344m	3317m
ν_s (NH ₂)	3284vs	3294s	3295s	3293s	3286s		3290m	3271m
ν_a (CH ₂)	2929vs	2970s	2970s	2958m	2958m	2920–2890s	2954s	2972m
ν_s (CH ₂)	2852vs	2894m	2891m	2900w	2900w		2902m	2949m
δ (NH ₂)	1597vs	1586s	1585s	1587s	1584s	1580s	1585s	1595s
δ (CH ₂)	1471m	1430w	1428w	1437w	1437w	1450m	1469w	1463m
ρ_ω (CH ₂)	1433m	–	–	–	–	–	1437w	1438vw
ρ_t (CH ₂)	1388m	1401vw	1403vw	1400vw	1400vw	1400w	1400vw	1403vw
ρ_t (NH ₂)	1351w	–	–	–	–	1320w	1432w	1342w
ρ_t (NH ₂)	1307vw	1298vw	1300vw	1300vw	1300vw	1270m	1273vw	1294m
ρ_t (NH ₂)	1267vw	nm	nm	nm	nm	nm	nm	nm
ρ_t (NH ₂)	–	–	–	–	–	–	–	1246vw
ν (Skeletal)	1093m	1093m	1095m	1098w	1099w	1160m	–	–
ν (Skeletal)	1066m	1055s	1059s	1058m	1058m	1090m	1084vw	1109vs
ν (Skeletal)	1008vw	–	–	–	–	1050m	1061m	1053w
ρ_ω (NH ₂)	–	986vs	983vs	981vs	982vs	1010s	nm	1012s
ρ_r (CH ₂) + ρ_ω (NH ₂)	–	912m	912m	912m	912m	1000w	985s	974vs
ρ_r (CH ₂)	843s	nm	nm	nm	nm	900m	912m	nm
Not assigned	738w	773w	770w	764vw	769vw	870w	nm	nm
ρ_r (NH ₂)	–	–	–	–	–	730w	771vw	771w
ρ_r (NH ₂)	nm	nm	nm	nm	nm	–	nm	748vw
δ (Skeletal)	520vw	–	–	–	–	670m	607m	652m
δ (Skeletal)	447	–	–	–	–	610m	–	–
						495s	510m,br	522m,br
						470w	nm	454w

^a Taken from Ref [6]. ^b Taken from Ref. [22] (only wavenumbers, not assignments). v = very, s = strong, w = weak, m = medium, nm = not measured.

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

Assignment	$\text{K}_2\text{Zn}(\text{CN})_4^a$	$\text{K}_2\text{Cd}(\text{CN})_4^a$	$\text{K}_2\text{Hg}(\text{CN})_4^a$	Cd-tn-Cd-Bz ^b	Cd-tn-Hg-Bz ^b
$\nu_1(\text{CN})A_1$	(2157)	(2149)	(2149)	(2172)	—
$\nu_5(\text{CN})F_2$	2152	2145	2146	2164vs	2162vs
Hot band	—	—	—	—	—
$\nu_2(\text{MC})A_1$	(347)	(327)	(335)	—	—
$\nu_6[\nu(\text{MC})+\delta(\text{NCM})]F_2$	359	316	330	348s	358s
$\nu_7[\nu(\text{MC})+\delta(\text{NCM})]F_2$	315	250	235	263w	254s
Assignment	Mn-tn-Cd-Bz ^b	Mn-tn-Hg-Bz ^b	Mn-tn-Zn-Bz	Zn-tn-Zn-Bz	
$\nu_1(\text{CN})A_1$	—	—	nm	(2198)	
$\nu_5(\text{CN})F_2$	2165vs	2163vs	2170vs	2192vs	
Hot band	—	—	2125vw	2156vw	
$\nu_2(\text{MC})A_1$	—	—	nm	nm	
$\nu_6[\nu(\text{MC})+\delta(\text{NCM})]F_2$	354s	360s	372s	373s	
$\nu_7[\nu(\text{MC})+\delta(\text{NCM})]F_2$	268w	265w	330m	350w	

* Raman bands are in parentheses.

^a Taken from Ref. [23].^b Taken from Ref. [6].

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

Assignment ^a	Liquid Benzene ^b	Cd-tn-Cd-Bz ^c	Cd-tn-Hg-Bz ^c	Mn-tn-Cd-Bz ^c	Mn-tn-Hg-Bz ^c	Mn-tn-Zn-Bz	Zn-tn-Zn-Bz
ν_8	(3166)	nm	nm	nm	nm	nm	nm
$\nu_{20}E_{1u}$	3073	3083w	3083m	3084w	3080w	3089w	3086w
$\nu_8 + \nu_{19}$	3075	3064w	3062w	3064w	3061w	3071w	3066w
$\nu_{13}B_{1u}$	3048	3028m	3028s	3031w	3028w	3035w	3032w
ν_2A_{1g}	(3062)	3064w	3062m	3064w	3061w	nm	nm
ν_7E_{2u}	(3050)	nm	nm	nm	nm	nm	(3063s)
		nm	nm	nm	nm	nm	(3048s)
$\nu_5 + \nu_{17}E_{1u}$	1955	1969w	1971w	1969w	1968w	1969w	1977vw
ν_8E_{2g}	(1586)	nm	nm	nm	nm	nm	1965w
							(1587m)
$\nu_{10} + \nu_{17}$	1815	1822w	1827w	1823w	1824w	1843vw	1836vw
$\nu_{19}E_{1u}$	1479	1479s	1476s	1478s	1477s	1826w	1820w
$\nu_{14}B_{2u}$	1309	nm	nm	nm	nm	1479s	1477s
ν_9E_{2g}	(1177)	nm	nm	nm	nm	1311w	1315w
$\nu_{15}B_{2u}$	1149	1151vw	1150vw	1150vw	1149vw	1168w	1168w
$\nu_{18}E_{1u}$	1036	1035m	1033m	1033m	1034m	1157w	1147w,sh
ν_1A_{1g}	(991)	(991vs)	(992vs)	nm	nm	1036m	1034m
ν_5B_{2g}	989	nm	nm	nm	nm	nm	(992vs)
$\nu_{17}E_{2u}$	966	nm	nm	nm	nm	nm	nm
$\nu_{10}E_{1u}$	(850)	nm	nm	nm	nm	nm	nm
$\nu_{11}A_{2u}$	670	700sh	695sh	697s	696sh	700s	692s
	nm	688vs	684vs	685vs	685vs	686vs	682vs
	nm	679sh	678sh	672sh	672sh	nm	nm

* Raman bands are in parentheses. ^a Taken from Ref. [27]. ^b IR bands from Ref. [26], Raman bands from Ref. [28]. ^c Taken from Ref. [6]. v = very, s = strong, w = weak, m = medium, sh = shoulder, nm = not measured.

We now direct attention to the tn ligand in the Zn-tn-Zn-Bz clathrate. The spectral appearance of the bands arising from the tn molecule in the infrared spectrum of the Zn-tn-Zn-Bz compound is found to be similar to that of the tn-chelated metal complex, $\text{Cu}(\text{tn})_2(\text{PF}_6)_2$ [21] (Table I), suggesting that the tn ligand molecule also behaves as a chelating ligand in our Zn-tn-Zn-Bz clathrate compound. Similar chelating arrangements have been shown for the chelated Hofmann-type, $\text{Cd}(\text{propylenediamine})\text{Ni}(\text{CN})_4 \cdot 0.5\text{ClCH}_2\text{CH}_2\text{Cl}$ [18] and $\text{Cd}(N\text{-methyl-1,3-diaminopropane})\text{Ni}(\text{CN})_4 \cdot 0.5\text{C}_6\text{H}_{12}$ [11], and chelated pn-Td-type, $\text{Cd}(\text{propylenediamine})\text{Cd}(\text{CN})_4 \cdot \text{ClCH}_2\text{CH}_2\text{Cl}$ [18] clathrates.

3.2. $\text{Zn}(\text{CN})_4$ GROUP VIBRATIONS

In the Td-type clathrates [8–10, 14] and Td-type host complexes [12] studied previously, the metal atom M in $\text{M}(\text{CN})_4$ is tetrahedrally surrounded by the carbon ends of four CN ions. Therefore, it is reasonable to assume that the complexes studied here also possess tetrahedral $\text{Zn}(\text{CN})_4$ groups. In assigning the bands attributable to $\text{Zn}(\text{CN})_4$ ions in the spectra of our compounds, we refer to the work of Jones [23] who presented vibrational data for the salt $\text{K}_2\text{Zn}(\text{CN})_4$ in the solid state. The structural studies on this salt have shown that the K—NC distance is ca. 2.9 Å [24], while the transition metal (M)—NC distances are ca. 2.3 Å in Hofmann-type host frameworks [25–27]. Hence, similar distances might also be expected in our compounds. Therefore, spectral data for $\text{K}_2\text{Zn}(\text{CN})_4$ can be used as references to account for the vibrational changes when the stiffer M—NC bonding takes place. The vibrational data for the $\text{M}(\text{CN})_4$ group in $\text{K}_2\text{Zn}(\text{CN})_4$ are given in Table II, together with the spectral data for $\text{Cd}(\text{CN})_4$ and $\text{Hg}(\text{CN})_4$ ions in some other clathrates for comparison with the assignments for the $\text{Zn}(\text{CN})_4$ group in our compounds. The assigned bands of the $\text{Zn}(\text{CN})_4$ group of the compounds appear to be much higher than those of $\text{Zn}(\text{CN})_4$ in the $\text{K}_2\text{Zn}(\text{CN})_4$ salt (Table II). Such upward frequency shifts have been observed for Td-type clathrates [2–6] and Td-type host complexes [13], in which both ends of the CN group are coordinated and explained as the mechanical coupling of the internal modes of $\text{M}(\text{CN})_4$ (M = Cd or Hg) with the M—NC (M = Mn or Cd) vibrations.

The wavenumber of ν_5 (2192 cm^{-1}) for Zn-tn-Zn-Bz appears to be much higher than that (2170 cm^{-1}) for the Mn-tn-Zn-Bz compound. Such a large difference in frequencies has not been noted for the Hofmann-type clathrate [28] and Hofmann-type host complexes [29]. Therefore, the difference may be mainly attributed to the conformational effect of the ligand molecule.

3.3. BENZENE VIBRATIONS

The assignments and the frequencies of the bands arising from the enclathrated benzene observed in the spectra of Mn-tn-Zn-Bz and Zn-tn-Zn-Bz compounds are

given in Table III, together with the frequencies of benzene in the liquid phase [30] and in some tn-Td-type clathrates [6] on which the assignments are based.

A number of papers have reported the vibrational spectra of benzene as a guest molecule for the Hofmann-type [28] and Td-type [2–6] clathrates. In these and in our spectra the spectral features are almost the same with the exception of the out-of-plane CH bending (ν_{11} , A_{2u}) vibration. This vibrational mode appears as a triplet for M(ethylenediamine) $M'(CN)_4 \cdot 2C_6H_6$ (M = Mn or Cd, $M' = Cd$ or Hg) [5], a doublet for our compounds and for Cd(pyrazine)M(CN) $_4 \cdot C_6H_6$ (M = Cd or Hg) [2], and $M(NH_3)_2M'(CN)_4 \cdot 2C_6H_6$ (M = Mn or Cd, $M' = Cd$ or Hg) [4], and a singlet for $M(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ (M = Mn, Fe, Ni, Cu, Zn and Cd) [28] and Cd(4,4'-bipyridyl) $M'(CN)_4 \cdot 2C_6H_6$ ($M' = Cd$ or Hg) [3]. In the case of clathrates with triplet or doublet features the splittings have been ascribed to crystal field effects (strong host–guest interactions) [2,4–6,28]. 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 [2]. Another feature of the ν_{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}). Similar shifts were observed for Hofmann-type [28] and Td-type [2–6] 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 tn ligand molecules of the host lattice, as has been suggested for other clathrates [2–6, 28]. 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 tn which have a more electrophilic character caused by the bidentate coordination.

The preceding discussion, considered as a whole, leads us to the conclusion that the host framework of the clathrates Mn-tn-Zn-Bz and Zn-tn-Zn-Bz are similar to those of the tn-Td-Type Cd-tn-Cd-Bz and the chelated pn-Td-Type Cd-pn-Cd-DCE, clathrates, respectively.

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