

Vibrational Spectroscopic Studies on the T_d -Type Clathrates: $M(\text{trimethylenediamine})M'(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ ($M=\text{Mn}$ or Cd , $M'=\text{Cd}$ or Hg)

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Abstract. IR spectra of $\text{Mn}(\text{C}_3\text{H}_{10}\text{N}_2)\text{M}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ ($M=\text{Cd}$ or Hg), and IR and Raman spectra of $\text{Cd}(\text{C}_3\text{H}_{10}\text{N}_2)\text{M}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ ($M=\text{Cd}$ or Hg) are reported. The spectral data suggest that the former two compounds are similar in structure to the latter two T_d -type clathrates.

Key words: Clathrates, inclusion compounds, trimethylenediamine, IR spectra, Raman spectra, benzene, tetracyano-cadmates, tetracyano-mercurates.

1. Introduction

In our previous works [1, 2] we reported that the IR and Raman spectral results suggest that the structure of $\text{Mn}(\text{NH}_3)_2\text{M}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ ($M=\text{Cd}$ or Hg) and $\text{Mn}(\text{en})\text{M}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ ($M=\text{Cd}$ or Hg , $\text{en}=\text{ethylenediamine}$) compounds are similar to those found in T_d -type clathrates given with a general formula $\text{Cd}(\text{II})\text{L}_2\text{M}(\text{II})(\text{CN})_4 \cdot n\text{G}$, where L_2 is a pair of unidentate ligand molecules such as NH_3 [3, 4] or a bidentate ligand molecule such as en [5, 6], 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 infinite $-\text{Cd}-\text{L}_2-\text{Cd}-\text{L}_2-$ chains extending along the a - and b -axes alternately, and tetrahedral $\text{M}(\text{CN})_4$ groups arranged between the consecutive crossing $-\text{Cd}-\text{L}_2-\text{Cd}-\text{L}_2-$ chains with the 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 [3, 4].

We have prepared two similar new compounds of the form $\text{Mn}(\text{trimethylenediamine})\text{M}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ ($M=\text{Cd}$ or Hg) (abbr. Mn-tn-M-Bz). In the present investigation we study the IR spectra of Mn-tn-Cd-Bz and Mn-tn-Hg-Bz (Raman spectra of these beige compounds could not be obtained by using the 488 nm or 515 nm laser line), and IR and Raman spectra of tn , $\text{Cd}(\text{tn})\text{Cd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ (abbr. Cd-tn-Cd-Bz) and $\text{Cd}(\text{tn})\text{Hg}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ (abbr. Cd-tn-Hg-Bz). For the latter two

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clathrates, a T_d -type structure has been indicated by the powder X-ray diffraction patterns, and the IR wave numbers of guest benzene molecules have been reported [7]. 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 *tn* chelated complexes. Such stabilities have been reported for the ethylenediamine cadmiumtetracyanocadmiate chelate [2, 6].

2. Experimental

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

The clathrates Mn-*tn*-M-Bz (M=Cd or Hg) were synthesized by adding slightly more than one millimole of *tn* 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 precipitate was filtered, washed with water, ethanol and ether, successively, and kept in a desiccator containing molecular sieves and saturated benzene vapour.

The clathrate compounds Cd-*tn*-Cd-Bz and Cd-*tn*-Hg-Bz were prepared by the method already reported [7].

The freshly prepared compounds were analyzed for Mn and Cd by AAS (Philips, Pu9200), and C, H and N by a CHN analyser (LECO, CHN-600) with the following results (found %/calculated %);

$Mn(C_3H_{10}N_2)Cd(CN)_4 \cdot 2C_6H_6$: Mn = 10.80/10.95, Cd = 22.79/22.40, C = 43.72/45.44, H = 4.66/4.42, N = 16.25/16.75.

$Mn(C_3H_{10}N_2)Hg(CN)_4 \cdot 2C_6H_6$: Mn=9.68/9.31, C=36.65/38.65, H=3.85/3.76, N=13.84/14.25.

These analytical results are often poor for the samples obtainable in powder form owing to partial decomposition. Such instability has been reported for other T_d -type clathrates having low boiling point guest species [7].

IR spectra of the compounds were recorded in the range of 4000 to 200 cm^{-1} using Perkin-Elmer 1300 and 621 spectrometers, which were calibrated with polystyrene and an indene/camphor/cyclohexane standard solution. The samples were prepared as mulls in Nujol and hexachlorobutadiene between CsI windows and as KBr discs. Raman spectra of the Cd-*tn*-Cd-Bz and Cd-*tn*-Hg-Bz clathrates (in powder form) in a home made spinning cell were excited using the 514.5 nm line of a Spectra-Physics Model 2016 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 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 clathrate

compounds with different crystal symmetry possibilities are not effective in significantly influencing the guest.

It will be convenient to divide the vibrations into three groups arising from tn ligands, from the $M(\text{CN})_4$ units and from the benzene moieties. The vibrational wavenumbers of the bands in the spectra of these species are tabulated in Tables I–III, respectively, along with some relevant spectral data for comparison. It should be noted that in the Raman spectra of the Cd-tn-Cd-Bz and Cd-tn-Hg-Bz clathrates, we could only detect the $\nu_1(A_1)$ band of the $M'(\text{CN})_4$ 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 tn molecule.

3.1. tn VIBRATIONS

Up to the time of writing, there have only been two relevant reports concerning the spectral data for the tn molecule. One by Segal and Eggerton [8] presents infrared spectral data for tn in solution in CCl_4 and in a KBr pellet in the frequency range of $4500\text{--}650\text{ cm}^{-1}$. In the other, Fleming and Shepherd presented infrared spectral data for the chelate complex $\text{Cu}(\text{tn})_2(\text{PF}_5)_2$ in the wavenumber 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 analyses [9].

The assignments and the wavenumbers of the fundamental bands assignable to the tn molecule in the spectra of the clathrate compounds studied are given in Table I, together with our spectral data for tn in solution in CCl_4 . The IR wavenumbers of our tn solution spectrum are in good agreement with those reported by Segal and Eggerton [8]. Our assignment is also often in agreement with that made for $\text{Cu}(\text{tn})_2(\text{PF}_5)_2$ [9].

IR spectral data for tn in the compounds studied would be expected to be consistent with all the characteristics of a coordinated ligand; that is, on coordination, the N—H and N—C stretching frequencies should decrease, while the C—H stretching frequency should increase, due to the consecutive inductive effects [10] (i.e., on coordination, N—H and N—C bonds should become weaker and C—H bonds should become stronger). But in our case, this expectation is not realized. This is possibly due to the hydrogen bonding as suggested below (see Section 3.3). This ambiguity was also observed in the spectra of *en*- T_d -type benzene clathrates [2].

Based on the present study, it is not possible to give an account of the conformation of the tn molecules in our clathrate compounds. However, some implication may be deduced from the structure of $\text{Cd}(\text{en})\text{Cd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$: X-ray diffraction studies have shown that the *en* molecules in $\text{Cd}(\text{en})\text{Cd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ are in a *gauche* conformation [6] due to the packing requirement for keeping the host framework of $\text{Cd}[\text{Cd}(\text{CN})_4]$ similar to the regular framework of Hofmann- T_d -type

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

Assignment	in CCl_4	Cd-tn-Cd-Bz	Cd-tn-Hg-Bz	Mn-tn-Cd-Bz	Mn-tn-Hg-Bz
$\nu_a(\text{NH}_2)$	3365s	3352s	3348s	3350s	3343s
$\nu_s(\text{NH}_2)$	3284s	3295s	3295s	3293s	3286s
$\nu_a(\text{CH}_2)$	2929vs	2970s	2970m	2958m	2958s
$\nu_s(\text{CH}_2)$	2852vs	2894m	2891m	2900w	2900w
$\delta_s(\text{NH}_2)$	1597s	1586s	1585s	1587s	1584s
$\delta_s(\text{CH}_2)$	1471mw	1430w	1428w	1437w	1437w
$\rho_w(\text{CH}_2)$	1388mw	1401vw	1403vw	1400vw	1400vw
$\rho_w(\text{NH}_2)$	1315vw	1298vw	1300vw	1300vw	1300vw
$\rho_t(\text{CH}_2)$	—	1118w	1120w	—	—
$\rho_w(\text{NH}_2)$	1093s	1093m	1095m	1098w	1099w
$\nu(\text{CN})$	1066s	1055s	1059s	1058m	1058m
	1006vw	986vs	983vs	981vs	982vs
$\nu(\text{CC})$	—	—	—	—	—
$\rho_r(\text{CH}_2)$	738w	773w	770w	764vw	769vw
	—	742w	742w	740vw	747w,sh
$\rho_r(\text{NH}_2)$	520vw	544s	540s	510m	513m
$\delta(\text{NCCN})$	447vw	456vw	450w	—	—

v=very, s=strong, w=weak, m=medium, sh=shoulder.

Table II. The vibrational wavenumbers (cm⁻¹) of the M'(CN)₄ group for the M-tn-Bz clathrates*.

Assignment	K ₂ Cd(CN) ₄ ^a	K ₂ Hg(CN) ₄ ^a	Cd-en-Cd-Bz ^b	Cd-en-Hg-Bz ^b	Mn-en-Cd-Bz ^b	Mn-en-Cd-Bz ^b
ν_1 (CN)A ₁	(2149)	(2149)	(2170vs)	(2175vs)	—	—
ν_5 (CN)F ₂	2145	2146	2167vs (2163sh)	2169vs (2168sh)	2168vs	2168vs
ν_2 (MC)A ₁	(327)	(335)	—	—	—	—
ν_6 [ν (MC)+ δ (NCM)]F ₂	316	330	354s	355s	352s	356s
ν_7 [ν (MC)+ δ (NCM)]F ₂	250	235	269w	270m	270w	268w
Assignment	Cd-tn-Cd-Bz		Cd-tn-Hg-Bz		Mn-tn-Cd-Bz	
ν_1 (CN)A ₁	(2171vs)	(2172vs)	—	—	—	—
ν_5 (CN)F ₂	2164vs	2162vs	2165vs	2163vs	—	—
ν_2 (MC)A ₁	—	—	—	—	—	—
ν_6 [ν (MC)+ δ (NCM)]F ₂	348s	358s	354s	360s	—	—
ν_7 [ν (MC)+ δ (NCM)]F ₂	263w	254s	268w	265w	—	—

* Raman bands are in parenthesis.

^a Taken from Ref. [1].^b Taken from Ref. [2].

v=very, s=strong, w=weak, m=medium, sh=shoulder.

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

Assignment ^a	Liquid Benzene ^b	Cd-en-Cd-Bz ^c	Cd-en-Hg-Bz ^c	Cd-tn-Cd-Bz	Cd-tn-Hg-Bz	Mn-tn-Cd-Bz	Mn-tn-Hg-Bz
ν_8	(3166)	—	—	—	—	—	—
$\nu_{20} E_{1u}$	3073	3085m	3086m	3083m	3083m	3084m	3080m
$\nu_8 + \nu_{19}$	3075	3066m	3064m	3064m	3062m	3064m	3061m
$\nu_{13} B_{1u}$	3048	3028s	3032s	3028s	3028s	3031s	3028s
$\nu_2 A_{1g}$	(3062)	3062vw	3060vw	3064m	3062m	3063m	3061m
		(3060s)	(3059s)	—	—	—	—
$\nu_7 E_{2g}$	(3050)	3042vw	3045vw	—	—	—	—
		(3044s)	(3044s)	—	—	—	—
$\nu_5 + \nu_{17} E_{1u}$	1955	1960w	1964w	1969w	1971w	1969w	1968w
$\nu_8 E_{2g}$	(1586)	1584m	(1585m)	—	—	—	—
$\nu_{10} + \nu_{17}$	1815	1818w	1820w	1822w	1827w	1823w	1824w
$\nu_{19} E_{1u}$	1479	1477s	1479s	1479s	1476s	1478s	1477s
$\nu_{14} B_{2u}$	1309	1309w	1310w	—	—	—	—
$\nu_9 E_{2g}$	(1177)	1176vw	1169vw	—	—	—	—
		(1176w)	(1175w)	—	—	—	—
$\nu_{15} B_{2u}$	1149	1147vw	1146vw	1151vw	1150vw	1150vw	1149vw
$\nu_{18} E_{1u}$	1036	1033m	1034m	1035m	1033m	1033m	1034m
$\nu_1 A_{1g}$	(991)	(992vs)	(992vs)	(991vs)	(992vs)	—	—
$\nu_5 B_{2g}$	989	—	—	—	—	—	—
$\nu_{17} E_{2u}$	966	—	—	—	—	—	—
$\nu_{10} E_{1g}$	(850)	853vw	849vw	—	—	—	—
$\nu_{11} A_{2u}$	670	695sh	700sh	700sh	695sh	697s	696sh
	—	683vs	688vs	688vs	684vs	685vs	685vs
	—	676sh	679sh	679sh	678sh	672sh	672sh
$\nu_6 E_{2g}$	—	604vw	601vw	—	—	—	—
	(607)	(605vw)	(606vw)	—	—	—	—

* Raman bands are in parenthesis. ^a Taken from ref. [20]. ^b IR bands from ref. [16], Raman bands from ref. [18]. ^c Taken from Ref. [2].
v=very, s=strong, w=weak, m=medium, sh=shoulder.

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) [3]. Therefore, the flexible *in* molecule is also expected to be in a *gauche* form in the clathrates studied.

3.2. $M'(\text{CN})_4$ ($M' = \text{Cd}$ OR Hg) VIBRATIONS

In order to assign the bands attributable to the $M'(\text{CN})_4$ group in the spectra of our clathrate compounds, it is appropriate to refer to the IR and Raman spectral data of the salts $\text{K}_2\text{Cd}(\text{CN})_4$ and $\text{K}_2\text{Hg}(\text{CN})_4$ in the solid form [11]. Structural studies have shown that the $\text{K}-\text{NC}$ distance is ca. 2.9 Å in $\text{K}_2\text{Cd}(\text{CN})_4$ [12] and $\text{K}_2\text{Hg}(\text{CN})_4$ [13], while the $\text{Cd}-\text{NC}$ distance is ca. 2.3 Å in T_d -type host frameworks [6]. Therefore, they can be used as references to account for the spectral changes when the stiffer $\text{Cd}-\text{NC}$ bonding takes place. The vibrational data for $\text{M}(\text{CN})_4$ groups in the clathrates studied are given in Table II, together with the IR and Raman wavenumbers of $\text{K}_2\text{Cd}(\text{CN})_4$ and $\text{K}_2\text{Hg}(\text{CN})_4$. Table II also lists the vibrational wavenumbers of the $M'(\text{CN})_4$ groups in $\text{M}(\text{en})M'(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ ($\text{M}=\text{Mn}$ or Cd , $M'=\text{Cd}$ or Hg) [2] for comparison. The wavenumbers assigned for the $M'(\text{CN})_4$ group in the clathrates studied appear to be much higher than those for the $\text{M}(\text{CN})_4$ ions in $\text{K}_2\text{M}(\text{CN})_4$ (Table II). Such frequency shifts have been observed for other T_d -type clathrates [12, 14, 15], in which both ends of the CN group are coordinated and explained as the mechanical coupling of the internal modes of $M'(\text{CN})_4$ with the metal (Mn or Cd)—NC vibrations [1]. It follows that the N-ends of the $M'(\text{CN})_4$ groups are also bound to an M (Mn or Cd) atom in our clathrate compounds.

3.3. BENZENE VIBRATIONS

The assignments and the wavenumbers of the vibrational bands of benzene observed in the IR and Raman spectra of the clathrate compounds studied are given in Table III, along with the wavenumbers of benzene in the liquid phase [16] and benzene in some clathrates [2] on which the assignments are based. The most structurally informative spectral features are the following:

All of the vibrational bands of the isolated benzene molecule are observed in the IR 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 because of the low site symmetry of the benzene molecules in the clathrate.

The CH out-of-plane mode (A_{2u}) in the IR spectra of the clathrates appears as a triplet (Table III). This vibrational mode also appears as a triplet for $\text{M}(\text{en})M'(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ ($\text{M}=\text{Mn}$ or Cd , $M'=\text{Cd}$ or Hg) [2], a doublet for $\text{Cd}(\text{pyrazine})\text{M}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ ($\text{M}=\text{Cd}$ or Hg) [14] and $\text{M}(\text{NH}_3)_2M'(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ ($\text{M}=\text{Mn}$ or Cd ; $M'=\text{Cd}$ or Hg) [1], and a singlet for $\text{M}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ ($\text{M}=\text{Mn}$, Fe , Ni , Cu , Zn or Cd) [17] and $\text{Cd}(4,4'\text{-bipyridyl})\text{M}(\text{CN})_4 \cdot \text{C}_6\text{H}_6$ ($\text{M}=\text{Cd}$ or Hg) [15]. In the case of clathrates with triplet and doubled features, the splitting is explained by the strong host–guest interactions (i.e., crystal field effects) [14]. In the case of clathrates with a single band, because of the larger cavities due to

the ligands, the host–guest interactions are not expected to be effective for splitting [15].

Another feature of the CH out-of-plane (A_{2u}) vibrational band is that it is found to be shifted to higher wavenumber from that of liquid benzene (Table III). Similar positive shifts have been observed for Hofmann-type [17, 18] and T_d -type clathrates [1, 2, 5, 14, 15]. This upward shift was explained for the Hofmann-type clathrates [17] by the presence of a weak hydrogen bond between π electrons located above and below the plane of the benzene ring and the ammonia molecules of the host lattice. The same was stated for other member of Hofmann-type [17–19] and T_d -type [1, 2] clathrates. Therefore, we reasonably suggest that the frequency shifts in our clathrates are explained by the partial π electron donation from the benzene ring to the hydrogen atoms of the triethylenediamine which has a more electrophilic character induced by the bidentate coordination.

The preceding discussion considered together leads us to the conclusion that the compounds $Mn(tn)Cd(CN)_4 \cdot 2C_6H_6$ and $Mn(tn)Hg(CN)_4 \cdot 2C_6H_6$ are similar in structure to the T_d -type clathrates $Cd(tn)M(CN)_4 \cdot 2C_6H_6$ ($M=Cd$ or Hg) [7].

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References

1. E. Kasap and Z. Kantarcı: *J. Incl. Phenom.* **20**, 33 (1995).
2. E. Kasap and Z. Kantarcı: *J. Incl. Phenom.* **23**, 1 (1995).
3. H. Yuge and T. Iwamoto: *J. Incl. Phenom.* **14**, 217 (1992).
4. R. Kuroda: *Inorg. Nucl., Chem. Lett.* **9**, 13 (1973).
5. T. Iwamoto and D.F. Shriver: *Inorg. Chem.* **11**, 2570 (1972).
6. S. Nishikiori and T. Iwamoto: *J. Incl. Phenom.* **3**, 283 (1985).
7. T. Iwamoto, M. Kiyoki, Y. Ohtsu and Y. Takeshige-Kato: *Bull. Chem. Soc. Jpn.* **51**, 488 (1978).
8. L. Segal and F.V. Eggerton: *Appl. Spectrosc.* **15**, 116 (1961).
9. G.D. Fleming and R.E. Shepherd: *Spectrochim. Acta* **43A**, 1141 (1987).
10. V. Gutmann: *Electrochim. Acta* **21**, 661 (1976).
11. L.H. Jones: *Spectrochim. Acta* **17**, 188 (1961).
12. B. Ziegler and D. Babel: *Z. Naturforsch.* **46B**, 47 (1991).
13. P.N. Gerlach and B.M. Powell: *J. Chem. Phys.* **85**, 6004 (1986).
14. N. Ekici, Z. Kantarcı and S. Akyüz: *J. Incl. Phenom.* **10**, 9 (1991).
15. S. Bayarı, Z. Kantarcı and S. Akyüz: *J. Incl. Phenom.* **17**, 291 (1994).
16. P.C. Painter and J.L. Koenig: *Spectrochim. Acta* **33A**, 103 (1977).
17. S. Akyüz, A.B. Dempster and R.L. Morehouse: *Spectrochim. Acta* **33A**, 1989 (1974).
18. J.E.D. Davies, A.B. Dempster and S. Suzuki: *Spectrochim. Acta* **30A**, 1183 (1974).
19. S. Suzuki, W.J. Orville-Thomas, A. Sopková and J. Skorsepa: *J. Mol. Struct.* **54** (1979).
20. E.B. Wilson: *Phys. Rev.* **45**, 706 (1934).