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Vibrational Spectroscopic Studies on the T_d-type Clathrates: M(*dl*-Propylenediamine)M'$(CN)_4$·nG

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In this study, M(*dl*-propylenediamine)M'$(CN)_4$·nG (M = Mn, M' = Zn or Hg; M = Cd, M' = Hg; $1.25 \leq n \leq 1.5$; G = thiophene) clathrates of *dl*-propylenediamine (pn) were prepared and their FT-IR and FT-Raman spectra were investigated. The infrared spectra of the clathrates were recorded in the range 4000-50 cm^{-1} and FT-Raman spectra of the clathrate (Cd-pn-Hg-Thi) was recorded 4000-50 cm^{-1} and its fundamental vibrational wavenumbers were obtained.

Key Words: *dl*-Propylenediamine, Infrared spectra, Raman spectra, Tetracyanometallate, Thiophene.

INTRODUCTION

The powder X-ray diffraction patterns of pn-T_d-type benzene clathrates[1] Cd(pn)M$(CN)_4$·1,5C_6H_6 (where pn = *dl*-propylenediamine, M = Cd or Hg) (Cd-pn-M-Bz) showed a close resemblance to those of the en-T_d-type clathrates[2] Cd(en)M$(CN)_4$·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. Such as a host framework, say in Cd(en)M$(CN)_4$·2C_6H_6, 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[3]. This structure provides two kinds of cavites, 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 is schematically illustrated[4,5] in Fig. 1. 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.

In our previous study we reported Hofmann T_d-type benzene clathrates for the *dl*-propylenediamine[6]. In this study we used thiophene (Thi) as a guest (G) molecule to produce new Hofmann T_d-type clathrates with the formula M(pn)M'$(CN)_4$·nG (where pn = *dl*-propylenediamine, G = thiophene, $1.25 \leq n \leq 1.5$, M = Mn, M' = Zn or Hg; M = Cd; M' = Hg). The aim of this study is to give further examples of Hofmann T_d-type clathrates and to present the vibrations of thiophene molecule in this structure. In order to understand the structures of the samples, the spectral data are correlated with those of the corresponding-T_d-type clathrates, the structures of which are known from single crystal X-ray studies[1,3].

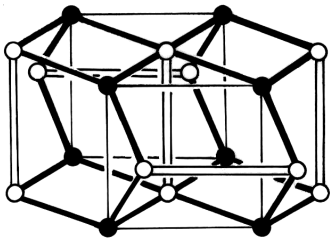

Fig. 1. Structural model of the pn-T_d-type host, $M(pn)M'(CN)_4$, open circle, 6-coordinate M; solid circle, tetragonal M'; open column, a pn ligand; thick line, CN bridge and thin line, edge of cavity

EXPERIMENTAL

The clathrates Mn-pn-M-Thi (M = Zn or Hg; Thi = thiophene) were synthesized by adding 1 mmol of pn and 1 mmol of $K_2M(CN)_4$ solution in water to 1 mmol of $MnCl_2$ solution in water saturated with thiophene. The clathrate compound Cd-pn-Hg-Thi was prepared by the similar method already reported for $Cd(pn)M(CN)_4\cdot 1.5C_6H_6$ (M = Cd or Hg) clathrates[6]. The freshly prepared samples were analyzed for C, H, N and S by a Carlo Erba 1108 elemental analyzer with the results as follows [found (calculated %)]: $Cd(C_3H_{10}N_2)Hg(CN)_4\cdot 1.5C_4H_4S$: C = 25.20 (25.28), H = 2.44 (2.61), N = 13.43 (13.61), S = 7.53 (7.78). $Mn(C_3H_{10}N_2)Zn(CN)_4\cdot 1.25C_4H_4S$: C = 35.66 (35.70), H = 3.58 (3.74), N = 20.55 (20.81), S = 9.43 (9.92). $Mn(C_3H_{10}N_2)$-$Hg(CN)_4\cdot 1.25C_4H_4S$: C = 26.63 (26.74), H = 2.67 (2.80), N = 15.43 (15.59), S = 7.27 (7.43).

The analytical results are often poor for the samples obtainable only in powder form owing to partial decomposition. These results suggest that the powder compounds with Mn originated from the expected compound with n = 1.5. Infrared spectra of the freshly prepared compounds were recorded between 4000 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 as KBr disks. Raman spectra were recorded using a Bruker RFS 100/S FT-Raman spectrometer in the range 4000-50 cm^{-1}. The 1064 nm line, provided by a Nd:YaG air-cooled laser, was used as excitation line.

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. The infrared and Raman spectra of Cd-pn-Hg-Thi clathrate are shown in Fig. 2. Because of the lack of structural data, the assignment was made by treating the propylenediamine, thiophene molecules and the $M'(CN)_4$ ions as isolated units. The wavenumbers and assignment of the observed bands in the infrared spectra of the compounds studied are given in Tables 1-3 for ligand pn, $M'(CN)_4$ groups and guest thiophene molecules, respectively, together with some pertinent spectral data for comparison.

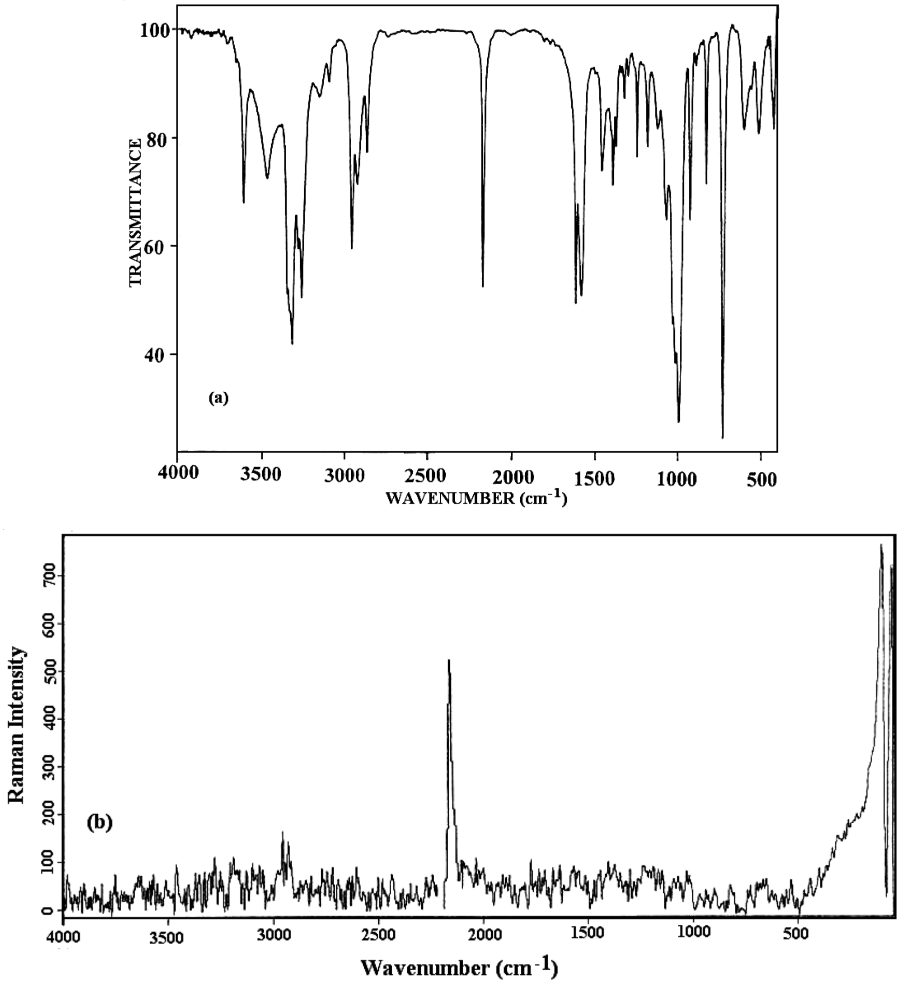

Fig. 2. The FT-IR (in KBr) (a) and FT-Raman (b) spectrum of the Cd-pn-Hg-Thi clathrate

Propylenediamine vibrations: The tentative assignments and the wavenumbers of the fundamental bands of pn observed in the spectra of the compounds under study are listed in Table-1. Most liquid aliphatic amines absorbs at 3400-3380 and 3330-3250 cm^{-1} with a shoulder near 3200 cm^{-1}. As seen in Table-1, four bands to NH stretching vibration of the NH_2 group in this region have been observed. The NH_2 group has its scissors deformation frequency at 1660-1590 cm^{-1}. It is observed that this mode at 1595 cm^{-1} in liquid pn, whereas this band in our clathrates is found to be shifting downward at 1581cm^{-1}. The CH_2 group gives rise to a near 1465 cm^{-1} owing to the scissoring vibrations while the asymmetric CH_3 deformation is also found around 1460 cm^{-1}. By comparison with the related molecules, a strong band at 1456 cm^{-1} in pn is assigned to CH_2 scissoring. The C-N stretching vibration occurs in the range 1220-1020 cm^{-1}. We observed several bands in this region and

TABLE-1
VIBRATIONAL WAVENUMBERS (cm^{-1}) OF
PROPYLENEDIAMINE IN M-pn-M'-Thi CLATHRATES

Assignment[a]	pn		Cd-Hg-Thi		Mn-Zn-Thi IR	Mn-Hg-Thi IR
	IR[a]	Raman	IR	Raman		
$\nu(NH_2)$	3361 s	3558 m	3353 m	3556 w	3348 w	3349 w
$\nu(NH_2)$	3292 s	3297 s	3321 m	3298 w	3319 m	3320 m
$\nu(NH_2)$	3272 s	–	3290 m	–	3286 w	3286 w
$\nu(NH_2)$	3182 s	–	3267 m	–	3266 m	3266 m
$\nu(CH_3)$	2960 vs	–	2961 m	2960 m	2955 m	2953 m
$\nu(CH_2)$	2929 s	–	2931 w	2931 m	2918 w	2917 w
$\nu(CH_2)$	2870 m	2897 vs	2873 m	–	2884 m	2886 m
$\nu(CH)$	2853 w	2858 vs	2850 vw	–	2850 vw	2852 vw
$\delta(NH_2)$	1595 vs	1591 vw	1585 s	1590 vw	1580 s	1581 s
$\delta(NH_2)$	–	–	1577 sh	–	1570 sh	1575 sh
(CH_2) sciss.	1456 m	–	1462 w	–	1463 w	1463 w
$\delta(CH_3)$	1433 vw	1435 w	1436 w	–	1433 w	1435 w
$\delta(CH_3)$	1377 m	–	1394 m	–	1396 vw	1395 vw
CH_2 wag.	1350 w	–	1376 m	–	1354 w	1342 vw
(NH_2) twist.	1252 vw	1291 w	-	–	-	-
(CH_3) rock	1144 w	–	1149 vw	–	1152 vw	1155 vw
ν(skeletal)	1093 s	–	1126 w	–	1126 w	1126 w
$\nu(CN)$	1066 w	1064 w	1072 m	–	1068 w	1081 s
$\nu(CN)$	1012 vw	–	1016 m	–	1018 m	1015 m
$\nu(CC)$	982 m, sh	–	995 m	–	998 m	997 m
NH_2 wag.	934 sh	905 vw	930 m	–	936 m	936 m
$\rho(CH_2) + \omega(NH_2)$	–	808 w	892 w	–	894 vw	894 vw
(CH_2) rock	619 vw	–	592 vw	–	618 vw	620 vw
δ(skeletal)	–	–	561 w	–	–	–
ν(skeletal) + ν(M-N)	509 vw	501 vw	516 m	–	518 m	518 m
δ(skeletal)	472 vw	402 w	438 vw	–	442 vw	440 vw

[a]Taken from[6]. The initial are: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder.

TABLE-2
VIBRATIONAL WAVENUMBERS (cm^{-1}) OF
CYANIDE GROUP FOR pn CLATHRATES

Assignment[a]	$K_2Zn(CN)_4$[a]	$K_2Hg(CN)_4$[a]	Cd-Hg-Bz[b]	Mn-Zn-Bz[b]	Cd-Hg-Thi	Mn-Zn-Thi	Mn-Hg-Thi
$\nu_1(CN)\ A_1$	(2157)	(2149)	(2171 vs)	–	(2169 vs)	–	–
$\nu_5(CN)\ F_1$	2152	2146	2166 vs	2173 vs	2177 vs	2174 vs	2174 vs
Hot band			2129 vw	2150 vw	2132 vw	2148 vw	2118 vw
$\nu_2(MC)\ A_1$	(347)	(335)	–	–	(336 w)	–	–
$\nu_6[\nu(MC)+\delta(NCM)]\ F_2$	359	330	350 s	375 s	352 s	375 s	354 s
$\nu_7[\nu(MC)+\delta(NCM)]\ F_2$	315	235	253 w	325 w	254 w	325 w	265 w

[a]Taken from[7], [b]Taken from[6]. The band observed in the Raman spectra are given parentheses. vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

TABLE-3
VIBRATIONAL WAVENUMBERS (cm^{-1}) OF
THIOPHENE IN M-pn-M'-Thi CLATHRATES

Assignment[a]	Liquid Thi.[a]	Cd-pn-Hg-Thi	Mn-pn-Zn-Thi	Mn-pn-Hg-Thi
A_1, ν(CH)	3107 m	3108 w	3106 w	3107 w
B_1, ν(CH)	3072 s	3068 vw	3065 vw	3066 vw
B_1, ($\nu_3 + \nu_{14}$)	1804 m	1814 vw	1812 vw	1814 vw
B_2, ($\nu_9 + \nu_{17}$)	1770 m	1791 vw	1793 vw	1793 vw
B_1, ν(CC)	1504 vw	1506 w	1506 vw	1505 vw
A_1, ν(CC)	1406 s	1409 vw	1409 w, sh	1409 w,sh
B_1, δ(CH)	1250 s	1251 w	1252 m	1250 m
A_1, δ(CH)	1081 s	1080 m	1080 m	1080 m
A_1, δ(CH)	1033 m	1031 m	1039 w,sh	1037 w,sh
B_1, [ν(ring) + δ(ring)]	868 w	860 w	851 w	853 w
A_1, δ(ring)	832 s	831 s	833 m	832 m
	–	814 w, sh	812 w,sh	813 w, sh
B_2, γ(CH)	712 vs	736 sh	738 sh	738 sh
		729 vs	729 vs	729 vs
A_1, δ(ring)	607 w	604 w	603 w	603 w
B_2, γ(ring)	453 w	455 w	457 w, sh	457 w, sh

[a]Taken from[10]. vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder.

assigned tentatively to C-N stretching vibrations of primary and secondary amine. In addition to the NH_2 wagging vibrations are found to shift downward for Cd-pn-Cd-Thi clathrate in comparison to the corresponding values in free ligand, whereas Mn-pn-M-Thi clathrates are found to be shift upward.

M'(CN)$_4$ (M' = Zn or Hg) group vibrations: In assigning the bands attributable to the M'(CN)$_4$ groups in the spectra of present compounds, it is appropriate to refer to the work of Jones, who presented vibrational data for the salts $K_2Zn(CN)_4$ and $K_2Hg(CN)_4$ in the solid phase[7]. The spectral data for M'(CN)$_4$ groups in the clathrate are given in Table-2, together with the vibrational wavenumbers of the $K_2Zn(CN)_4$ and $K_2Hg(CN)_4$ salts[7]. Table-2 also lists the wavenumbers of the infrared spectra of the M'(CN)$_4$ (M = Zn or Hg) units in the Mn-pn-Zn-Bz and Cd-pn-Hg-Bz clathrates[6] for comparison. Such frequency shifts have been observed for other T_d-type clathrates[6,8,9], in which both ends of the CN group are coordinated and explained as the mechanical coupling of the internal modes of M'(CN)$_4$ with the M-NC vibrations. It follows that the N-ends of the M'(CN)$_4$ groups are also bound to a M atom in present clathrates compounds. Another notable feature is that ν_5 is at a higher frequency for Cd (2177 and 2169 cm^{-1} for FT-Raman) than for Mn (2174 cm^{-1}), suggesting that the strength of the Cd-N bond is higher that of the Mn-N bond. This is due to the fact that the second ionization potential of Cd is higher than that of Mn.

Thiophene vibrations: Thiophene is a molecule belonging to the point group C_{2v} and a group analysis shows that there are eight A_1 (in-plane), seven B_1 (in-plane), three A_2 (out-of-plane) and three B_2 (out-of-plane) modes. In the infrared spectra, some out-of-plane modes of thiophene are observed together with the in-plane A_1 and B_1 modes.

In general, the frequencies found are close to those of liquid thiophene[10]. In present clathrates, the γ(CH) out-of-plane hydrogen deformation mode in the spectra of the clathrates are found to shift to higher frequency (Table-3) from that of liquid thiophene (712 cm^{-1}). This band is assigned to the CH out-of-plane vibrations shifted 20 cm^{-1} above the liquid state frequency. The corresponding band of pure thiophene is very strong in the infrared spectra. In spectra of the clathrates, the same is found. Similar positive shifts have been observed for Hofmann-type thiophene 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 propylenediamine ligand molecules of the lattice, as has been suggested for other clathrates[11,12]. Therefore, it is reasonable to suggest that the frequency shifts in present clathrates are due to the π electrons donation from the thiophene ring to the hydrogen atoms of the NH groups in the propylenediamine, which have a more electrophlic character caused by the bidentate coordination.

Another essential feature of the out-of-plane CH bending vibration (B_2) is that it appears as a doublet (Table-3). This vibrational mode also appears as a singlet for $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_4H_4S$ and a doublet for $Cd(NH_3)_2Ni(CN)_4 \cdot 2C_4H_4S$. In the case of benzene clathrates with doublet and triplet features, splitting have been ascribed to crystal field effects[11] (strong host-guest interactions). In pure thiophene, however, where the symmetry is lower, the B_2 out-of-plane ring vibration is active and is observed at 453 cm^{-1} with weak intensity in the infrared spectrum of the liquid state. In present infrared spectra of the thiophene clathrates, this band is observed at 457 cm^{-1}. If the large shift to higher frequency of the CH out-of-plane vibration is caused by the interaction between guest molecule and lattice, as discussed above, it would not necessarily affect all the out-of-plane vibrations, but only the CH out-of-plane vibrations. Unfortunately it could not confirm this by observing other out-of-plane vibrations, since the A_2 vibrations are infrared inactive, presumably because they were too weak.

It should be noted that, in these clathrates, the number of guest molecules is between 1.5 and 1.25. The decrease in the number of guest molecules from 2 in Hofmann-T_d-type[6,8,9] to 1.5 in the present series is due to the fact that the α-cavites may be occupied by the pn molecules and the β-cavites may be occupied by the guest molecule[1,13]. A similar number has been found in Hofmann-diam-type clathrates[1,6]. To conclude we can report that thiophene molecule in these clathrates has acted as a guest molecule. The preceeding discussion considered Mn-pn-Zn-Thi and Mn-pn-Hg-Thi are similar to those of the pn-T_d-type, Cd-pn-Hg-Thi clathrate compound.

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