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Vibrational Spectroscopic Studies on the T_d-type N,N'-dimethylethylenediamine(II)tetracyanometallate(II) Benzene Clathrates

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FT-IR spectra of Mn(DMEDA)M$(CN)_4 \cdot C_6H_6$ (M = Zn, Cd or Hg; DMEDA = N,N'-dimethylethylenediamine) and FT-IR and FT-Raman spectra of Cd(DMEDA)M$(CN)_4 \cdot C_6H_6$ (M = Cd or Hg) are reported. All the vibrational modes of coordinated DMEDA are characterized. The spectral features suggest that these compounds are similar in structure to the Hofmann-T_d-type clathrates.

Key Words: Benzene, Inclusion compounds, N,N'-Dimethylethylenediamine, Hofmann-T_d-type clathrates, Infrared spectra, Raman spectra.

INTRODUCTION

We are currently involved in the preparation and spectroscopic structural description of the T_d-type clathrate compounds, which are derived from the original benzene clathrates[1] Cd(en)M$(CN)_4 \cdot 2C_6H_6$ (en = ethylenediamine, M = Cd or Hg) by through appropriate replacements of the host moieties[2-6]. Such a host framework, in Cd(en)M$(CN)_4 \cdot 2C_6H_6$, 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 bounds to the Cd atoms[7]. 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 the Hofmann-type hosts, while the β cavity is a twisted biprism, as has been demonstrated in previous papers[8,9].

Guest-host interactions in these clathrates provide an explanation for the effects of enclathrates on the structural and spectroscopic properties of both the guest and the host molecules. The nature of the guest-host interactions[10] varies from charge transfer forces to hydrogen bonding and to weak van der Waals interactions. We have now prepared 5 similar new compounds Mn(DMEDA)M$(CN)_4 \cdot C_6H_6$ (M = Zn, Cd or Hg and Cd(DMEDA)M$(CN)_4 \cdot C_6H_6$ (M = Cd or Hg) in powder form. In the present investigation we study the FT-IR spectra of Mn(N,N'-dimethyl ethylenediamine) M$(CN)_4 \cdot C_6H_6$ (abbr. Mn-DMEDA-M; M = Zn, Cd or Hg) and FT-IR and FT-Raman spectra of the Cd(DMEDA)M$(CN)_4 \cdot C_6H_6$ (M = Cd or Hg; abbr. Cd-DMEDA-M) compounds. In order to understand the structures of the samples, the spectral data are correlated with those of the corresponding-T_d-type clathrates[7,9].

EXPERIMENTAL

All chemicals used were reagent grade (Merck) and used without further purification. The clathrates Mn-DMEDA-M-Bz (M = Zn, Cd or Hg) were synthesized by adding one millimole of DMEDA 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 molecular sieve and saturated benzene vapour. The clathrate compounds Cd-DMEDA-Cd-Bz and Cd-DMEDA-Hg-Bz were prepared by the methods already described in references[2,3].

The freshly prepared compounds were analyzed for C, H and N by a LECO CHNS-932 analyzer with the following results (found/calculated %). The analytical results were agreement with the proposed formula.

$Cd(C_4H_{12}N_2)Cd(CN)_4 \cdot C_6H_6$: C = 33.07/33.96, H = 3.91/3.66, N = 16.01/16.97
$Cd(C_4H_{12}N_2)Hg(CN)_4 \cdot C_6H_6$: C = 28.24/28.82, H = 3.25/3.11, N = 14.21/14.40
$Mn(C_4H_{12}N_2)Zn(CN)_4 \cdot C_6H_6$: C = 42.88/43.04, H = 4.72/4.64, N = 21.43/21.51
$Mn(C_4H_{12}N_2)Cd(CN)_4 \cdot C_6H_6$: C = 38.23/38.41, H = 4.09/4.14, N = 19.13/19.20
$Mn(C_4H_{12}N_2)Hg(CN)_4 \cdot C_6H_6$: C = 31.57/31.97, H = 3.27/3.45, N = 15.79/15.98

The FT-IR spectra were recorded between 4000 and 400 cm^{-1} on Perkin Elmer 1330 and Mattson 1000 FT-IR spectrometers, which were calibrated using indene and polystyrene film. The samples were prepared as mulls in nujol and KBr pellets. Raman spectra of the Cd-DMEDA-Cd-Bz and Cd-DMEDA-Hg-Bz clathrate compounds (in powder form) in a home-made spinning cell were excited 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. A liquid nitrogen cooled Ge detector was used. The output laser power was set to 40-60 mW.

RESULTS AND DISCUSSION

The FT-IR and FT-Raman spectra of the $Cd(DMEDA)Cd(CN)_4 \cdot Bz$ clathrate are shown Figs. 1 and 2, respectively. The spectral features of the compounds under study are found to be similar to each other, suggesting that they have similar structural features. It may be convenient to divide the vibrations into three groups and arising from the N,N'-dimethylethylenediamine ligands, $M'(CN)_4$ groups and guest molecule benzene, respectively. The assignments and wavenumbers of the observed bands in the infrared and Raman spectra of the compounds studied are given in Tables 1-3 for ligand N,N'-dimethylethylenediamine, $M(CN)_4$ groups and guest benzene molecules, respectively, together with some pertinent spectral data for comparison.

N,N'-Dimethylethylenediamine vibrations: The fundamental vibrational modes of the N,N'-dimethylethylenediamine, assigned by Scott *et. al.*[11], are presented in Table-1. This molecule belongs to C_2 point group and there will be 48 modes of vibrations. The highest frequency modes are N-H stretches. It has been shown in the literature[11,12] that DMEDA without hydrogen bonding has an N-H stretch of 3371 cm^{-1} and DMEDA with hydrogen bonding has an N-H stretch of 3341 cm^{-1}.

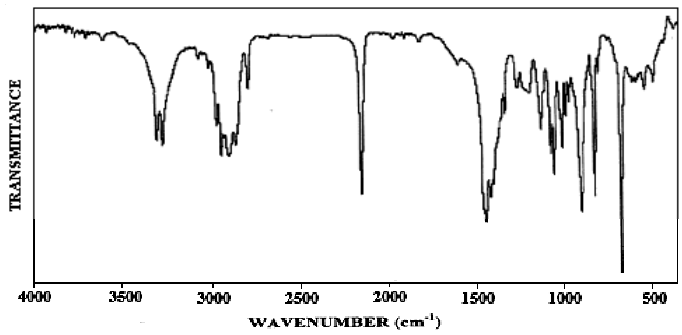

Fig. 1. FT-IR (in KBr) spectra of $Cd(DMEDA)Cd(CN)_4 \cdot C_6H_6$ clathrate

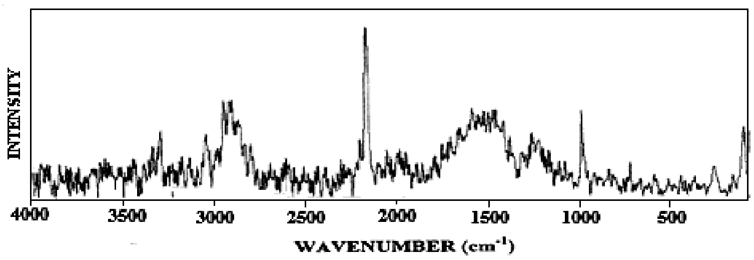

Fig. 2. FT-Raman spectra of $Cd(DMEDA)Cd(CN)_4 \cdot C_6H_6$ clathrate

The N-H stretching frequencies of the DMEDA molecules in the compounds are found to be higher than those of DMEDA in liquid (Table-1). The N-H stretching frequencies in the FT-IR spectra are 3333 and 3305 cm^{-1} and in the Raman spectra are 3328 and 3292 cm^{-1}, which indicates that hydrogen bonding is present in the clathrates. The absence of the splitting of these sharp bands implies the bidentate coordination of the ligand DMEDA molecule in the clathrates. Infrared spectral data for DMEDA 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 consecutive inductive effects[8]. In other words, on coordination, N-H and C-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 is observed for the N-H stretching vibrations (Table-1). This ambiguity is also observed in the spectra of tn-T_d-type[2], pn-T_d-type[3] and en-T_d-type[5,10] benzene clathrates.

As seen from Table-1, the CH_2 and CH_3 stretching vibrations modes are observed IR bands at 2971 and 2816 cm^{-1} in the clathrates. The similar bands observed FT-Raman bands at 2971 and 2894 cm^{-1} correspond to these vibrations. The N-H parallel bending mixed with methyl antisymmetric deformation mode is assigned to band in FT-IR at 1444 cm^{-1} and at FT-Raman spectra 1450 cm^{-1} in free DMEDA ligand. We clearly observed these modes in FT-IR at 1456 cm^{-1} (strong band) and FT-Raman

TABLE-1
THE VIBRATIONAL WAVENUMBERS (cm^{-1}) OF N,N'-DIMETHYLETYLENEDIAMINE IN THE M-DMEDA-M'-Bz (M = Mn or Cd; M' = Zn, Cd or Hg) CLATHRATES

Assignment[a]	DMEDA[a]		Cd-Cd-Bz		Cd-Hg-Bz		Mn-Zn-Bz	Mn-Cd-Bz	Mn-Hg-Bz
	IR	Raman	IR	Raman	IR	Raman	IR	IR	IR
N-H stretch	3323	3327	3333 m	3326 m	3333 m	3327 m	3334 m	3336 m	3339 m
N-H stretch	3280	3290	3305 m	3292 m	3304 m	3292 m	3302 m	3301 m	3303 m
CH_2 stretch; CH_3 stretch	2967	2970	2971 s	2963 m	2971 s	2961 m	2970 s	2970 s	2971 s
CH_2 stretch	2934	2939	2926 s	2929 m	2926 s	2927 m	2922 s	2922 s	2924 s
CH_2 stretch; CH_3 stretch	2887	2891	2888 m	2915 m	2889 m	2915 m	2887 m	2886 m	2892 m
CH_3 stretch	2840	2843	2817 w	2818 w	2816 w	2819 w	2817 w	2816 w	2819 w
C-H stretch	2788	2790	–	–	–	–	–	–	–
CH_2 stretch	2681	2679	–	–	–	–	–	–	–
CH_2 scissors, methyl as sym def.	1473	1473	1469 s	1518 w	1467 s	1518 w	1469 s	1471 s	1463 s
N-H bend, methyl as sym def.	1444	1450	1457 s	1450 w	1456 s	1450 w	1455 s	1454 s	1455 s
Methyl sym. def. CH_2 deform.	1418	1420	1419 w	1410 w	1419 w	1412 w	1419 w	1400 w	1415 w
CH_2 wag	1361	1363	–	1377 w	–	1377 w	1354 w	1376 w, sh	1375 w, sh
CH_2 wag	1346	1347	1350 vw	–	1351 vw	–	1352 vw	1353 w	1353
CH_2 twist	1251	1255	1281 w	1290 w	1282 w	1288 w	1281 w	1283 vw	1280 w
C-N stretch	1151	1152	1150 m	–	1150 m	–	1150 m	1150 m	1153 m
C-N stretch	1122	1124	1134 w, sh	1112 w	1135 w, sh	1111 w	1132 w, sh	1132 w	1132 w
C-N stretch	1106	1113	1091 m	1095 w	1091 m	106 w	1093 m	1091 m	1091 m
CH_2 rock	1042	1039	–	-	-	–	–	–	–
C-C stretch	1022	1021	1029 w	–	1029 w	–	1028 w	1028 w	1029 w
Methyl wag	985	990	922 s	–	923 s	–	923 s	921 s	923 vs
CH_2 rock	879	881	847 s	839 w	850 s	840 w	850 s	850 s	850 vs
N-H ⊥ bend	789	805	789 w	821 vw	788 w	823 vw	791 w	790 vw	788 vw
N-H ⊥ bend	736	–	no	719 w	no	720 w	770 w	770 w	-
C-N-C bend (out-of-phase)	–	559	556 m	581 w	555 m	581 w	557 w	557 w	555 m
C-N-C bend (in-phase)	545	542	505 m	496 vw	505 m	496 vw	512 vw	514 vw	512 vw
C-N-C bend (out-of-phase)	448	425	441 m, sh	428 vw	444 m, sh	430 vw	455 w	451 vw	454 vw
C-N-C bend (out-of-phase)	–	395	–	–	–	–	–	–	–
C-N-C bend (out-of-phase)	–	360	–	–	–	–	–	–	–
C-N-C bend (out-of-phase)	–	345	–	342 w	–	348 w	–	–	–
Methyl twist	–	268	–	264 vw	–	259 vw	–	–	–
Methyl twist	–	243	–	–	–	–	–	–	–

[a] Taken from ref.[11], vs: very strong, s: strong, m: medium, w: weak, vw: very weak, sh: shoulder.

TABLE-2
THE VIBRATIONAL WAVENUMBERS (cm^{-1}) OF THE M'(CN)$_4$ GROUP FOR THE M-DMEDA-M'-Bz CLATHRATES*

Assignment[a]	$K_2Zn(CN)_4$[a]	$K_2Cd(CN)_4$[a]	$K_2Hg(CN)_4$[a]	Cd-Cd-pn-Bz[b]	Cd-Hg-pn-Bz[b]
ν_1(CN) A_1	(2157)	(2149)	(2149)	(2171 s)	(2171 s)
ν_5(CN) F_1	2152	2145	2146	2166 vs (2167 m)	2166 vs (2167 m)
Hot band				2133 vw	2129 vw
ν_2(MC) A_1	(347)	(327)	(335)	–	–
$\nu_6[\nu(MC) + \delta(NCM)]F_2$	359	316	330	363 s	350 s
$\nu_7[\nu(MC) + \delta(NCM)]F_2$	315	250	235	253 w	253 w
	Cd-Cd-Bz	Cd-Hg-Bz	Mn-Zn-Bz	Mn-Cd-Bz	Mn-Hg-Bz
ν_1(CN) A_1	(2178 vs)	(2179 vs)	–	–	–
ν_5(CN) F_1	2170 vs	2170 vs	2171 vs	2171 vs	2171 vs
Hot band	2132 vw	2138 vw	2133 vw	2137 vw	2136 vw
ν_2(MC) A_1	(316 w)	(325 w)	–	–	–
$\nu_6[\nu(MC) + \delta(NCM)]F_2$	370 s	371 s	370 s	371 s	371 s
$\nu_7[\nu(MC) + \delta(NCM)]F_2$	254 w	325 w	254 w	325 w	325 w

*: Raman bands are in parentheses, [a]Taken from ref.[13], [b]Taken from ref.[3], vs: very strong, s: strong, m: medium, w: weak, vw: veryweak, and sh: shoulder.

TABLE-3
THE VIBRATIONAL WAVENUMBERS (cm^{-1}) OF BENZENE IN THE M-DMEDA-M'-Bz CLATHRATES*

Assignment[a]	Liquid benzene[b]	Cd-pn-Cd-Bz[c]	Cd-pn-Hg-Bz[c]	Cd-Cd-Bz	Cd-Hg-Bz	Mn-Zn-Bz	Mn-Cd-Bz	Mn-Hg-Bz
$\nu_8 + \nu_{19}$	3075	3065 w	3065 w	3074 w	3075 w	3078 w	3078 w	3078 w
ν_{20}, E_{1u}	3073	3086 m	3086 m	3090 m	3091 m	3099 m	3099 m	3099 m
ν_{13}, B_{1u}	3062	3032 m	3031 m	3033 m	3033 m	3041 m	3041 m	3041 m
ν_2, A_{1g}	(3059)	no	no	(3074 m)	(3074 m)			
$\nu_5 + \nu_{17}$, E_{1u}	1955	1967 w	1969 w	1972 w	1974 w	1973 vw	1974 vw	1974 vw
$\nu_{10} + \nu_{17}$	1815	1824 w	1825 w	1829 w	1830 w	1831 vw	1830 vw	1830 vw
ν_8, E_{2g}	(1596)	no	no	(1584 m)	(1585 m)			
ν_{19}, E_{1u}	1479	1477 s	1476 s	1479 s	1477 s	1479 s	1477 s	1477 s
ν_{14}, E_{2u}	1309	1305 vw	1305 vw	1306 vw	1306 vw	1309 w	1307 w	1309 w
ν_9, E_{2g}	(1178)	no	no	obs	obs			
ν_{15}, B_{2u}	1149	no	no	1149 w	1149 vw	1149 vw	1147 vw	1147 vw
ν_{18}, E_{2u}	1036	1032 s	1034 s	1032 s	1034 s	1036 s	1037 s	1035 s
ν_1, A_{1g}	(992)	(992 vs)	(992 vs)	(993 m)	(993 m)			
ν_{10}, E_{1g}	(849)	no	no	(843 w)	(843 w)			
ν_{11}, A_{2u}	670	694s,sh 683 vs	694 s,sh 684 vs	694 vs	694 vs	692 vs	692 vs	693 vs
ν_6, E_{2g}	(606)	no	no	(608 w)	(609 w)			

*Raman bands are in parentheses, [a]Taken from ref.[25], [b]IR bands from ref.[20], Raman bands from ref.[22], [c]Taken from ref.[3], vs: very strong, s: strong, m: medium, w: weak, vw: very weak, sh: shoulder and no: not observed.

spectra at 1450 cm^{-1} (weak band) in the clathrates. The CH_2 wagging mode is observed in both FT-IR 1351 cm^{-1} and in FT-Raman 1350 cm^{-1} in the clathrates. These weak bands at 1151, 1122 and 1106 cm^{-1} (IR) are attributed to C-N stretching mode of free DMEDA. These bands in the clathrates are observed at 1150, 1135 and 1091 cm^{-1} lower frequencies compared with the free DMEDA. On the other hand, the methyl wagging band is observed at 922 cm^{-1} lower frequency in the clathrates compared with the liquid DMEDA. The frequencies in DMEDA of 789 and 736 cm^{-1} for the N-H bend are slightly shifted to higher frequencies region for the clathrates. Finally, the C-N-C bend (out-of-phase) modes appeared at 545 and 448 cm^{-1} in DMEDA ligand. These bands are observed at 505 cm^{-1} in the FT-IR spectra (*ca.* 496 and 428 cm^{-1} in FT-Raman) of the their clathrates, respectively. Similarly, the C-N-C bend (in-phase) modes appeared at 441 cm^{-1} in the clathrates.

M'(CN)$_4$ group vibrations: In assigning the bands attributable to M'(CN)$_4$ (M = Zn, Cd or Hg) ions in the spectra of present compounds, we refer the work of Jones[13] 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 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-2). Such frequency shifts have been observed for other T_d-type clathrates[2-6,10,14-16] and T_d-type host complexes[17,18], 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. It follows that the N-ends of the M'(CN)$_4$ groups are also bound to a M atom in present clathrate compounds.

Benzene vibrations: Vibrational spectral data for benzene in a number of T_d-type clathrates have been presented[2-6,10,14,15]. The assignment and the frequencies of the vibrational bands of benzene observed in the infrared and Raman spectra of the compounds are given in Table-3. This table also lists the wavenumbers of benzene in the liquid phase[19] and in the clathrates[3] Cd-pn-Cd-Bz, on which the assignments are based. The most structurally informative spectral features are the following.

The CH out-of-plane mode (A_{2u}) in the spectra of the clathrates are found to be shifted to higher frequency (692 cm^{-1}) from that of liquid benzene (670 cm^{-1}). Similar positive frequency shifts were observed for Hofmann-type[20-22] and T_d-type[2-6,10,16] clathrates. Akyuz *et al.*[20] explained 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 ammonia molecules of the host lattice. Therefore, we may reasonably suggest that the frequency shifts in present clathrate compounds are due to the π-electron donation from the benzene ring to the hydrogen atoms of the ligand molecule which has a more electrophilic character caused by the essential coordination.

Another essential feature of the out-of-plane C-H bending vibration (A_{2u}) is that it appears as a very intense single band at *ca.* 692 cm^{-1} in the infrared spectra of the clathrate compounds (Table-3). A similar single band was observed[14] for Cd(4,4'-bipyridyl)M(CN)$_4$·2C$_6$H$_6$ (M = Cd or Hg). 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[15].

Based on the present spectral data, it is not possible to determine the orientation of the benzene molecules in the host lattice in our clathrate compounds. As mentioned previously, the relative orientation of the N-H bands of ligand with respect to the axis of the π cloud of benzene must be the one most favourable for the hydrogen bonding[24]. The preceding discussion, considered as a whole, leads us to the conclusion that the host lattice of our clathrates are similar to those of the other T$_d$-type clathrates.

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