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Vibrational Spectroscopic Studies on the en-Td-Type Benzene Clathrates: M(ethylenediamine)M'(CN)$_4$·2C$_6$H$_6$ (M=Mn or Cd, M'=Cd or Hg)

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Abstract. IR spectra of Mn(en)M(CN)$_4$·2C$_6$H$_6$ (M=Cd or Hg), and IR and Raman spectra of Cd(en)M(CN)$_4$·2C$_6$H$_6$ (M=Cd or Hg) clathrates are reported. The spectral features suggest that the first two compounds are similar in structure to the later two Td-type clathrates.

Key words: en-Td-type clathrate, inclusion compounds, ethylenediamine, IR spectra, Raman spectra.

1. Introduction

ESR spectral studies have shown that the host framework of the en-Td-type benzene clathrate compound Cd(en)M(CN)$_4$·2C$_6$H$_6$, where en is ethylenediamine and M is Cd or Hg, is a good reservoir for the cyclohexadienyl, C$_6$H$_7$·, radical which is thermally unstable in γ-irradiated neat benzene or solutions of benzene in common organic solvents [1]. In these compounds the host framework is formed from the infinite -Cd-en-Cd-en- chains extending along the a- and b-axes alternately and the tetrahedral M(CN)$_4$ moieties arranged between the consecutive crossing -Cd-en-Cd-en- chains with the connections of the N-ends at the Cd atoms in the chains [2, 3]. This structure provides two kinds of cavities, α and β, for the guest benzene 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 illustrated in a number of previous papers [1, 2, 4]. The clathrate compounds having this type of host structure reported to date have only been confined to those with a Cd metal atom in the octahedral environment [1–5].

Kasap and Kantarci [5] recently prepared two novel Td-type benzene clathrates, Mn(NH$_3$)$_2$M(CN)$_4$·2C$_6$H$_6$ (M=Cd or Hg) and presented some vibrational spectral data. Now we have prepared two new ethylenediaminemanganese(II)tetracyano-metallate(II) benzene(1/2) clathrates, Mn(en)M(CN)$_4$·2G (M=Cd or Hg, G=benzene;

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abbreviated to Mn-en-M-2G), for the first time. Our aim in this paper is to throw light on the structure of these compounds in powder form by the spectral correlation between these and Cd-en-Cd-2G for which the structure is known [3]. In this study the IR spectra of $Mn(en)Cd(CN)_4 \cdot 2C_6H_6$ and $Mn(en)Hg(CN)_4 \cdot 2C_6H_6$, and the IR and Raman spectra of $Cd(en)Cd(CN)_4 \cdot 2C_6H_6$ and $Cd(en)Hg(CN)_4 \cdot 2C_6H_6$, (abbreviated to Cd-en-Cd-2G and Cd-en-Hg-2G, respectively) clathrates are reported. The Raman spectra of the former two compounds (light brown) could not be obtained by using 488 or 515 nm laser lines. A previous paper by Iwamoto and Shriver gives very limited vibrational data with tentative assignments for the latter two compounds [2].

2. Experimental

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

The clathrates Mn-en-Cd-2G and Mn-en-Hg-2G were prepared by adding slightly more than one millimole of ethylenediamine and one millimole of $K_2M(CN)_4$ (M=Cd or Hg) solution in water to one millimole of $MnCl_2$ solution in water saturated with benzene. The brown 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-en-Cd-2G and Cd-en-Hg-2G were prepared by the method already described in Ref. [2].

The freshly prepared compounds were analyzed for Mn and Cd by AAS (Philips, PU 9200), and C, H and N by a CHN analyser (LECO, CHN-600) with the following results (found %/calculated %): $Mn(C_2H_8N_2)Cd(CN)_4 \cdot 2C_6H_6$: Mn=11.41/11.26, Cd=23.26/23.05, C=44.03/44.29, H=3.97/4.13, N=16.81/17.23. $Mn(C_2H_8N_2)Hg(CN)_4 \cdot 2C_6H_6$: Mn=9.87/9.54, C=36.24/37.51, H=3.38/3.50, N=13.97/14.59.

IR spectra of the compounds were recorded in the range of 4000 to 200 cm^{-1} on Perkin-Elmer 1330 and 621 spectrometers, which were calibrated using 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. The Raman spectra of the Cd-en-Cd-2G and Cd-en-Hg-2G compounds (in powder form) in a home-made spinning cell were excited using the 514.5 nm line of a Spectra-Physics Model 2016-Ar$^+$ ion laser and recorded on a Jobin-Yvon U1000 spectrometer which was calibrated against the laser plasma emission lines.

3. Result and Discussion

The clathrate compounds studied show no major difference in the IR spectra between the nujol (or hexachlorobutadiene) mulls and KBr pellet. The similarities between the IR and Raman spectral features of the clathrate compounds suggest

that they also have similar structural features. These, in turn, suggest that the degrees of interactions of the benzene, en ligand and $M(CN)_4$ species with their surroundings are almost the same for each clathrate. It will be most convenient to divide the vibrations into three groups arising from the ethylenediamine ligands, from the $M(CN)_4$ units and from the benzene moieties, respectively. The vibrational wavenumbers of the bands in the spectra of these species are tabulated in Tables I–III, respectively, together with some relevant spectral data for comparison.

The prototype of the studied compounds, Cd-en-Cd-2G, crystallises in the non-centrosymmetric space group $P4_222$ (D_4^5) with $Z = 2$ [3]. This means all the chemical entities in the crystal are theoretically non-centrosymmetric. The en in this single crystal structure is disordered [3] so that the application of the correlation method appears not to be effective for the en molecule. The site symmetries of $M(CN)_4$ and benzene are D_2 and C_2, respectively [6]. The correlation diagram for the point groups of $M(CN)_4$ (T_d) and benzene (D_{6b}) with the factor group D_4, through sites D_2, and C_2, respectively, is shown in Figure 1. Figure 1 indicates that the effect of low site symmetries on the degenerate modes of $M(CN)_4$ and benzene species should, in principle, be observed in the infrared and Raman spectra in the form of splitting, but, no indication of such splittings could be observed in the spectra at room temperature (Tables II and III). The absence of splittings in the spectra suggests that the magnitudes of the splittings are too small to permit resolution. As can be seen from the correlation diagram (Figure 1), the effect of low site symmetry on the vibrational activities is only valid for the benzene moieties. Some infrared active modes under the site symmetry are weakly observed (Table III) as discussed below.

3.1. VIBRATIONS OF ETHYLENEDIAMINE

The assignments and the wavenumbers of the vibrational bands of en observed in the spectra of the clathrate compounds under study are given in Table I, together with the spectral data for en in the liquid phase [8] on which the assignments are based. Our assignments for the localized vibrations are in good agreement with those reported previously for Cd-en-Cd-2G and Cd-en-Hg-2G [2].

In the gas phase, Yokozeki and Kuchitsu [9] have shown that the en molecule possesses conformational isomerism and that the dominant form (more than 95%) is the *gauche* conformation. This gives the molecule C_2 symmetry. The IR and Raman spectral data (depolarization ratios, frequency shifts and group frequencies correlations) for the en molecule and its deuterated derivatives in the liquid and solid phases have been reported to be in accord with the *gauche* and *trans* conformations, respectively [8]. From the results of IR spectroscopic and powder X-ray difraction data [7] the en ligand molecules in Cd(en) $M(CN)_4 \cdot 2C_6H_6$ (M=Ni or Pd) were suggested to have a *trans* form, while the single crystal X-ray difraction studies have shown that the en molecules in Cd-en-Cd-2G are in a *gauche* conformation [3]. The *gauche* form may be due to the packing requirement for keeping the host

TABLE I. The vibrational wavenumbers (cm^{-1}) of ethylenediamine in M-en-M'-2G clathrates.

Assignment[a]	Liquid en[a]		Cd-en-Cd-2G		Cd-en-Hg-2G		Mn-en-Cd-2G	Mn-en-Hg-2G
	IR	Ra	IR	Ra	IR	Ra	IR	IR
ν(NH$_2$), B	3349vs	3355m	3316	3316m	3318m	3315m	3314m	
ν(NH$_2$), A	3279vs	3290vs	3283w	3287s	3285w	3286s	3283w	3283w
	3189ms	3185m	nm	nm	nm	nm	nm	nm
ν(CH$_2$), B	nm	2904sh	2974w	nm	2974w	nm	2970w	2970w
ν(CH$_2$), A	2922vs	2925vs	2943m	2943s	2945m	2943m	2949m	2950w
	2853vs	2852vs	2881w	nm	2882w	nm	2880w	2879w
δ(NH$_2$), A, B	1595vs	1599mw	1590s	nm	1591s	nm	1596s	1593vs
δ(NH$_2$), A, B	nm	nm	1574vs	1578w	1574vs	1577w	1576vs	1574vs
δ(CH$_2$), A, B	1458mw	1478s	1458m	1457w	1458m	1456w	1460m	1458m
ω(CH$_2$), A, B	1356mw	1359m	1383vw	nm	nm	nm	1384vw	1382vw
t(NH$_2$), A, B	1254vw	1242w	nm	nm	nm	nm	nm	nm
ν(skeletal), A	1096m	1100s	1072vs	nm	1073vs	nm	1078vs	1080vs
ν(skeletal), B	1054mw	1062w	nm	nm	nm	nm	nm	nm
ν(skeletal), A	991sh	987m	nm	nm	nm	nm	nm	nm
ω(NH$_2$), A	900vs	nm	991vs	nm	990vs	nm	994vs	993vs
τ(CH$_2$), A	nm	880sh	nm	nm	nm	nm	nm	nm
ρ(CH$_2$), ω(NH$_2$), A	830m	838s	769vw	773s	768vw	772s	770vw	768w
δ(NCCN), B	513mw	512vw	502s	nm	505s	nm	508s	507s
δ(NCCN), A	475w	475m	nm	nm	nm	nm	445m	447w
(CN) torsion, A, B	nm	340m	nm	nm	nm	nm	nm	nm
(CC) torsion, A, B	nm	180sh	nm	nm	nm	nm	nm	nm

[a] Taken from ref. [8].

v = very, s = strong, w = weak, m = medium, sh = shoulder, nm = not measured.

TABLE II. Cyanide group vibrational wavenumbers (cm^{-1}) for the M-en-M'-2G clathrates.

Assignment	$K_2Cd(CN)_4$ [a]		$K_2Hg(CN)_4$ [a]		Cd-pyz-Cd-G[b,c]		Cd-pyz-Hg-G[b,c]	
	IR	Ra	IR	Ra	IR	Ra	IR	Ra
$\nu_1(CN)A_1$	–	2149	–	2149	–	2180vs	–	2180vs
$\nu_5(CN)F_2$	2145	–	2146	–	2176vs	2172sh	2176vs	2172sh
Hot band ?	–	–	–	–	2164vw	2162vw	2165vw	2162vw
$\nu_2(MC)A_1$	–	327	–	335	–	354vw	–	354vw
$\nu_6[\nu(MC)$ $+\delta(NCM)]F_2$	316	–	330	–	365vs	–	368vs	–
$\nu_7[\nu(MC)$ $+\delta(NCM)]F_2$	250	–	235	–	–	–	–	–

Assignment	Cd-en-Cd-2G		Cd-en-Hg-2G		Mn-en-Cd-2G	Mn-en-Hg-2G
	IR	Ra	IR	Ra	IR	IR
$\nu_1(CN)A_1$	–	2170vs	–	2175vs	–	–
$\nu_5(CN)F_2$	2167vs	2163sh	2169vs	2168sh	2168vs	2168vs
Hot band ?	2135vw	–	–	–	2132vw	–
$\nu_2(MC)A_1$	–	–	–	–	–	–
$\nu_6[\nu(MC)$ $+\delta(NCM)]F_2$	354s	–	355s	–	352s	356s
$\nu_7[\nu(MC)$ $+\delta(NCM)]F_2$	269w	–	270m	–	270w	268w

[a,b] Taken from Refs. [10 and 14], respectively.
[c] Cd(pyrazine)Cd(CN)$_4\cdot$C$_6$H$_6$.
[d] Cd(pyrazine)Hg(CN)$_4\cdot$C$_6$H$_6$.
v = very, s = strong, w = weak, m = medium, sh = shoulder.

framework of Cd[Cd(CN)$_4$] similar to the regular framework of Td-type clathrates Cd(NH$_3$)$_2$Cd(CN)$_4\cdot$2C$_6$H$_6$ and Cd(NH$_3$)$_2$Hg(CN)$_4\cdot$2C$_6$H$_6$ [4]. The fact that en has the *gauche* form in Cd-en-Cd-2G and the spectral similarities between Cd-en-Cd-2G and the other clathrate compounds under study suggests that the en ligands in Cd-en-Hg-2G, Mn-en-Cd-2G and Mn-en-Hg-2G compounds also have *gauche* (δ) forms. For the *gauche* configuration and consequent C_2 symmetry, all vibrational modes are IR or Raman active.

3.2. M(CN)$_4$ (M=Cd OR Hg) GROUP VIBRATIONS

In assigning the bands attributable to the M(CN)$_4$ (M=Cd or Hg) ion in the spectra of our clathrate compounds we refer to the work of Jones who presented vibrational data for the salts K$_2$Cd(CN)$_4$ and K$_2$Hg(CN)$_4$ in the solid phase [10]. The structural studies on these salts have shown that the K—NC distance is ca. 2.9 Å in K$_2$Cd(CN)$_4$ [11] and K$_2$Hg(CN)$_4$ [12] while the Cd—NC distance is ca. 2.3 Å in Td-type host structures [3, 4, 13]. Therefore, they can be used as references to

TABLE III. The vibrational wavenumbers (cm^{-1}) of benzene in the M-en-M'-2G clathrates.

Assignment[a]	Liquid Benzene IR[b]	Ra[c]	Cd-pyz-Cd-G[d,e] IR	Ra	Cd-pyz-Hg-G[d,f] IR	Ra	Cd-en-Cd-2G IR	Ra	Cd-en-Hg-2G IR	Ra	Mn-en-Cd-2G IR	Mn-en-Hg-2G IR
$2\nu_8$	—	3166	—	3163vw	—	nm	—	nm	—	nm	—	—
ν_{20} E$_{1u}$	3073	—	3088s	—	3088s	—	3085m	—	3086m	—	3080m	3082m
$\nu_8 + \nu_{19}$	3075	—	—	—	—	—	3066m	—	3064m	—	3061w	3062m
ν_{13} B$_{1u}$	3048	—	3068m	—	3068m	—	3028s	—	3032s	—	3025s	3029s
ν_2 A$_{1g}$	—	3062	—	3062m	—	3062m	3062vw	3060s	3060vw	3059s	3061vw	3058vw
ν_7 E$_{2g}$	—	3050	—	3053sh	—	3053sh	3042vw	3044s	3045vw	3044s	3040vw	3041vw
$\nu_5 + \nu_{17}$ E$_{1u}$	1955	—	1951w	—	1951w	—	1960w	—	1964w	—	1959w	1960w
ν_8 E$_{2g}$	—	1586	—	1586m	—	1586m	—	1584m	—	1585m	—	—
$\nu_{10} + \nu_{17}$	1815	—	—	—	—	—	1818w	—	1820w	—	1814w	1815w
ν_{19} E$_{1u}$	1479	—	1479m	—	1479m	—	1477s	—	1479s	—	1474s	1474s
ν_{14} B$_{2u}$	1309	—	—	—	—	—	1309w	—	1310w	—	—	—
ν_9 E$_{2g}$	—	1177	—	1177m	—	1177m	1176vw	1176w	1169vw	1175w	1172vw	1173vw
ν_{15} B$_{2u}$	1149	—	1147sh	—	1147sh	—	1147vw	—	1146vw	—	1150vw	1148vw
ν_{18} E$_{1u}$	1036	—	1035m	—	1035m	—	1033m	—	1034m	—	1032m	1032m
ν_1 A$_{1g}$	—	991	—	991vs	—	991vs	—	992vs	—	992vs	—	—
ν_5 B$_{2g}$	989	·	—	—	—	—	—	—	—	—	—	—
ν_{17} E$_{2u}$	966	—	975vw	—	974vw	—	—	—	—	—	—	—
ν_{10} E$_{1g}$	—	850	—	855w	—	854vw	853vw	nm	849vw	nm	848vw	848vw
ν_{11} A$_{2u}$	670	—	685vs	—	685vs	—	695sh	—	700sh	—	689sh	688sh
	—	—	681vs	—	681vs	—	683vs	—	688vs	—	676vs	680vs
	—	—	—	—	—	—	676sh	—	679sh	—	668sh	668sh
ν_6 E$_{2g}$	—	607	—	605	—	608	604vw	605	601vw	606	602vw	603vw

[a] Taken from Ref. [22]. [b] Taken from Ref. [18]. [c] Taken from Ref. [19]. [d] Taken from Ref. [14]. [e] Cd(pyrazine)Cd(CN)$_4$·C$_6$H$_6$. [f] Cd(pyrazine)Hg(CN)$_4$·C$_6$H$_6$.

v = very, s = strong, w = weak, m = medium, sh = shoulder, nm = not measured.

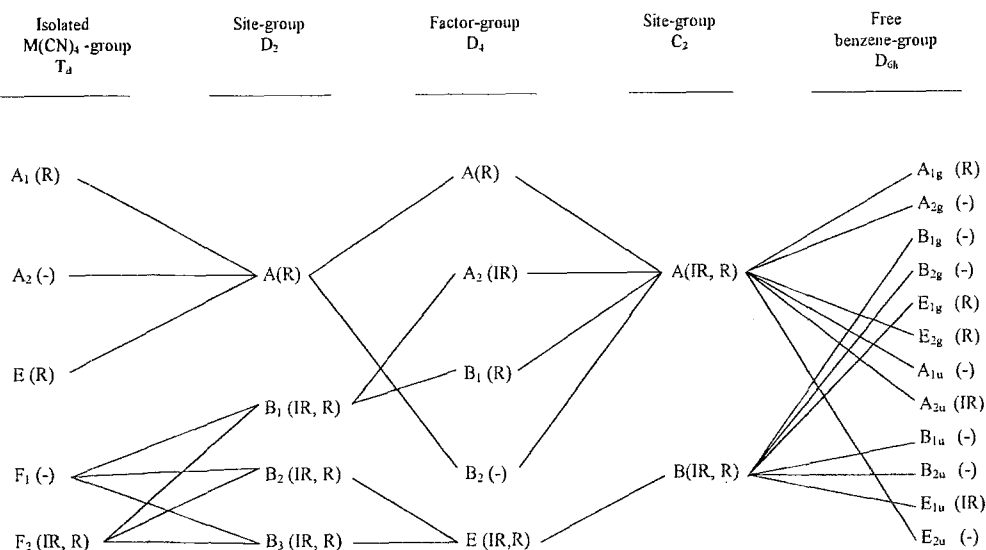| Isolated M(CN)₄ -group T_d	Site-group D_2	Factor-group D_4	Site-group C_2	Free benzene-group D_{6h}

Fig. 1.   Correlation diagram for the symmetry species of the M(CN)₄ ion and benzene molecule in the Cd-en-Cd-2G clathrate. R = Raman active; IR = Infrared active; – = inactive.

account for the vibrational changes when the stiffer Cd—NC bonding takes place [14]. The vibrational data for M(CN)₄ groups in the compounds studied are given in Table II together with the vibrational wavenumbers of $K_2Cd(CN)_4$ and $K_2Hg(CN)_4$. In Table II is also listed the wavenumbers of the IR and Raman spectra of the benzene clathrates $Cd(pyrazine)Cd(CN)_4 \cdot C_6H_6$ and $Cd(pyrazine)Hg(CN)_4 \cdot C_6H_6$ [14] for comparison.

The assigned wavenumbers for the M(CN)₄ group in the compounds under study appear to be much higher than those for isolated M(CN)₄ units (Table II). Such frequency shifts have been observed for other Td-type clathrates, $M(NH_3)_2M'(CN)_4 \cdot 2C_6H_6$ (M=Mn or Cd, M′=Cd or Hg) [5], $Cd(pyrazine)M'(CN)_4 \cdot C_6H_6$ (M′=Cd or Hg) [14], $M(4,4'-bipyridyl)M'(CN)_4 \cdot 2C_6H_6$ (M=Mn or Cd: M′=Cd or Hg) [15] and Td-type host complexes $M(pyridine)_2M'(CN)_4$ (M=Mn or Cd; M′=Cd or Hg) [16, 17], 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=Cd or Hg) with the metal (Cd—NC) vibrations [5, 14–17].

3.3. VIBRATIONS OF BENZENE

The benzene molecule in the structure of Cd-en-Cd-2G is on the C_2 site, and, in principle, all vibrational selection rules for the free benzene molecule (D_{6h}) are lost (Figure 1). The other clathrates studied may also be expected to have similar symmetry properties, since their spectral features are very similar.

The assignments and the wavenumbers of the bands arising from the enclathrated benzene observed in the IR and Raman spectra of Cd-en-Cd-2G, Cd-en-Hg-2G,

Mn-en-Cd-2G and Mn-en-Hg-2G clathrates are given in Table III, together with the wavenumbers of benzene in the liquid phase [18, 19] and in some clathrates [14] on which the assignments are based. The most outstanding spectral features are the following.

All of the vibrational bands of the free benzene 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 due to the low site symmetry (Figure 1) of each of the two benzene molecules in the clathrate. The CH out-of-plane vibrational band (A_{2u}) in the IR spectra of the clathrate compounds appears as a triplet (Table III). This vibrational mode appears as a doublet for Cd(pyrazine)M′$(CN)_4$·C_6H_6(M′=Cd or Hg) [14] and M$(NH_3)_2$M′$(CN)_4$·$2C_6H_6$ (M=Mn or Cd, M′=Cd or Hg) [5] and a singlet for Hofmann-type clathrates M$(NH_3)_2$Ni$(CN)_4$·$2C_6H_6$ (M=Mn, Fe, Ni Cu, Zn or Cd) [20], and Td-type clathrates Cd(4,4′-bipyridyl)M′$(CN)_4$·C_6H_6 (M′=Cd or Hg) [5, 15]. In the case of clathrates with doublet and in our case with triplet features, the splittings are due to 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 expected not to be effective for splitting. Another feature of the CH out-of-plane (A_{2u}) vibrational band is that it is found to be shifted to higher frequency (Table III) from that of liquid benzene (670 cm^{-1}). Similar positive shifts were observed for Hofmann-type [18–20] and Td-type [2, 5, 14, 15] clathrates. This upward shift was explained for the Hofmann-type clathrates [20] 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 members of Hofmann-type [19–21] and Hofmann-Td type [5] clathrates. 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 ethylenediamine which has a more electrophilic character caused by the bidentate coordination.

The preceeding discussion considered as a whole leads us to draw the conclusion that the clathrates Cd-en-Hg-2G, Mn-en-Cd-2G and Mn-en-Hg-2G are similar in structure to the en-Td-type clathrate Cd-en-Cd-2G.

Acknowledgements

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