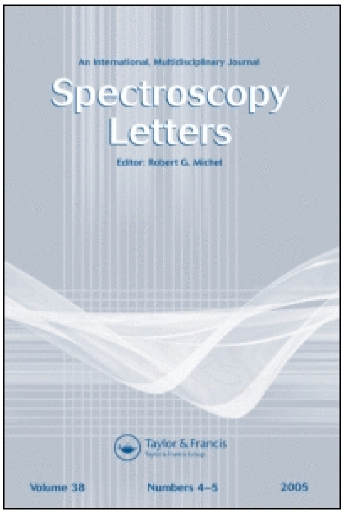

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VIBRATIONAL SPECTROSCOPIC STUDIES ON THE 1,4-DIAMINOBUTANE-T^d-TYPE CLATHRATES: Cd(dabn)M$(CN)_4$ $\cdot 1{,}5C_6H_6$ (M=Cd or Hg)

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VIBRATIONAL SPECTROSCOPIC STUDIES ON THE 1,4-DIAMINOBUTANE-T_d-TYPE CLATHRATES: $Cd(dabn)M(CN)_4 \cdot 1{,}5C_6H_6$ (M = Cd OR Hg)

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ABSTRACT

Two new title compounds have been prepared in powder form and their vibrational spectra are reported. Spectral data suggest that the host frameworks of these compounds are similar to those of the en-T_d-type Cd(ethylenediamine)$M(CN)_4 \cdot 2C_6H_6$ (M = Cd or Hg) clathrates.

Key Words: Diaminobutane; Clathrates; Infrared; Raman

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INTRODUCTION

Single crystal X-ray diffraction studies have shown that the host frame- work of the $Cd(en)M(CN)_4 \cdot 2C_6H_6$ (en = ethylenediamine, M = Cd or Hg) clathrate is formed from the -Cd-en-Cd-en- chains extending along the a- and b-axes alternately and the tetrahedral $M(CN)_4$ groups arranged between the consecutive crossing -Cd-en-Cd-en- chains with the connections of the N-ends at the Cd atoms in the chains.[1,2] 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 cavities is a twisted biprism, as has been illustrated in a number of previous papers.[1,3–5]

In previous studies a number of clathrate compounds possessing this type of host structure have been reported.[1–11] Now, for the first time, we have prepared the title compounds (abbr. Cd-dabn-M-Bz) in powder form. In concerning with the structural features of the Hofmann-type or T_d-type clathrates and host complexes which can only be prepared in powder form,[6–13] vibrational spectroscopy has been recognized to be a value in such structural elucidation. In this study, the infrared and Raman spectra of Cd-dabn-Cd-Bz and Cd-dabn-Hg-Bz clathrate compounds are reported. The spectra of the host complexes Cd-dabn-M (M = Cd or Hg) are also presented for comparison. The spectral data are structurally correlated with that of the en-T_d-type clathrates, $Cd(en)M(CN)_4 \cdot 2C_6H_6$ (M = Cd or Hg).[1,2,7]

EXPERIMENTAL

The clathrate compounds were prepared by the similar method already reported for $Cd(tn)M(CN)_4 \cdot 2C_6H_6$ (M = Cd or Hg) clathrates.[8] They were synthesized by adding one millimole of dabn and one millimole of $K_2M(CN)_4$ solution in water to one millimole of $CdCl_2$ in water saturated with benzene. The precipitate was filtered washed with water, ethanol and ether, successively, and kept in a desiccator containing saturated guest vapour. The infrared spectra of the compounds as mulls in nujol and hexachlorobutadiene between CsI plates were recorded in the range of 4000 to 400 cm^{-1} on Mattson 1000 FTIR spectrometers. The Raman spectra of the samples in a home-made spinning cell were excited using a 488 nm or 515 nm line of Spectra-Physics Model 2016-4S argon ion laser and recorded on a Jobin-Yvon U 1000 spectrometer, which was calibrated against the laser plasma emission lines. The freshly prepared compounds were analysed for C, H and N by a LECO CHNS 932 analyser. The analytic results agree with the proposed formula.

RESULTS AND DISCUSSION

Owing to the lack of structural data, the assignment was made by treating the 1,4-diaminobutane and benzene moieties and the $M(CN)_4$ groups as isolated units. The vibrational wavenumber of the bands in the spectra of these species are tabulated in Tables 1–3, respectively, along with some relevant spectral data for comparison. It should be noted that in the Raman spectra of the samples, we could only detected the strongest $\nu_1(A_1)$ bands of $M(CN)_4$ groups and guest benzene molecule (Table 3). This is due to the occurrence of fluorescence of high intensity and the relatively low scattering cross-section of the dabn molecule.

Kasap and Özçelik[14] reported infrared spectral data for 1,4-diaminobutane in liquid phase and in the Hofmann-type clathrates of the form $M(dabn)Ni(CN)_4 \cdot 1{,}5C_6H_6$ (M = Fe, Co, Ni or Cd). X-ray studies have shown that the dabn molecule in the latter compounds acts as bridging bidentate ligand in cis-trans conformation.[15]

The tentative assignments and the wavenumbers of the fundamental bands of dabn observed in the spectra of the compounds under study are listed in Table 1. For the purposes of comparison and discussion, Table 1 also includes spectral data for liquid en[16] and Cd-en-Cd-Bz,[7] dabn in solution in CCl_4 and in $Cd(dabn)Ni(CN)_4$.1,5 aniline clathrate.[14]

When the spectra of the compounds under study are compared with the spectrum of the $Cd(dabn)Ni(CN)_4 \cdot 1{,}5$aniline, where diamine acts as bridging bidentate ligand in cis-trans conformation, it can be seen that this show similarities in their most frequencies although there are a number of intensity differences. This is evidence for the compounds containing bringing bidentate ligands, with the nitrogen atoms bounded to the consecutive Cd atoms.

Based on the present spectral data, it is not possible to give an account on whether the dabn molecules in our compounds are in cis-, trans- or gauch-conformation. However, some implication may be deduced from the structure of $Cd(en)Cd(CN)_4 \cdot 2C_6H_6$ clathrate: X-ray diffraction studies have shown that the en molecule in this clathrate is in gauch conformation[17] due to the packing requirement for keeping the host framework of $Cd[Cd(CN)_4]$ similar to the regular framework of the Hofmann-T_d-type clathrates $Cd(NH_3)_2Cd(CN)_4 \cdot 2C_6H_6$ (M = Cd or Hg).[1] Therefore, the flexible dabn molecule is also expected to be in a gauch form in the clathrates studies here. Another notable is that on comparing the spectra of dabn in Cd-dabn-M- (M = Cd or Hg) clathrates with those of Cd-dabn-M-(M = Cd or Hg) host complexes, it is seen that there are due to the host-guest interaction or a different bonding arrangement of ligand dabn molecule around the octahedral M atom of the host complexes, such

Table 1. The Vibrational Wavenumbers (cm^{-1}) of 1,4-Diaminobutane in the M-dabn-M′-Bz Clathrates

Assignment	Liquid en[a]	dabn in CCl_4	Cd-en-Cd-2Bz[b]	Cd-Ni-An[c]	Cd-Cd-Bz	Cd-Hg-Bz	Cd-Cd	Cd-Hg
$\nu(NH_2)$	3349 vs	3390 s	3316 m	3348 s	3348 m	3350 m	3345 m	3346 m
							3336 m	3336 m
$\nu(NH_2)$	3279 vs	3326 s	3283 vs	3283 s	3292 m	3296 m	3292 m	3292 m
							3159 m	3147 m
$\nu(CH_2)$	2922 vs	2930 s	2929 s	2952 s	2942 w	2945 w	2966 m	2964 m
		2912 msh		2915 m	2920 w	2923 w	2947 m	2939 m
							2931 m	2929 m
$\nu(CH_2)$	2853 vs	2870 m	2881 w	2882 m	2889 w	2887 w	2897 w	2904 w
		2851 s		2850 s	2858 w	2858 w	2889 m	2877 m
							2862 w	2858 w
$\delta(NH_2)$	1595 vs	1606 s	1590 s	1590 s	1583 s	1587 s	1595 s	1583 s
			1574 vs	no	no	no	1579 s	no
$\delta(CH_2)$	1458 vw	1464 s	no	no	1473 m	1464 w	1469 s	1466 s
		1456 s	1458 m	1461 m	1446 w	1448 vw	1450 w	1443 w
$\rho_w(CH_2)$	1356 vw	1378 m	1383 vw	1377 vw	1375 m	1375 m	1380 m	1373 w
		1366 sh	no	1365 sh	1365 sh	1365 sh	1365 sh	1358 w
$\rho_t(CH_2)$	–	1335 w	no	1313 vw	1311 vw	1311 vw	no	no
		1308 w	no	no	1279 vw	1279 vw	1290 w	no
$\rho_t(NH_2)$	1254 vw	no	no	no	1257 vw	1257 vw	1261 w	1259 m
			no	no	1236 vw	1236 vw	1200 m	1223 w
ν(skeletal)	1096 m	1145 vw	no	1166 vw	1111 m	1109 vw	1141 m	1140 m
ν(skeletal)	1054 vw	1070 m	1072 vs	1065 w	1082 w	1082 m	1110 s	1097 s
ν(skeletal)	–	no	no	1051 w	1055 m	1055 m	1051 s	1057 m
ν(skeletal)	991 sh	no	no	no	1022 m	1024 m	1040 sh	1038 m
$\rho_w(NH_2)$	900 vs	954 w	no	1001 m	997 m	999 m	1018 w	1014 vw
$\rho_r(CH_2)$	–	878 m,br	no	no	974 w	974 vw	991 w	967 w
		863 m,br	no	941 vw	958 m	958 m	968 s	962 s
			no	no	931 w	924 m	921 w	916 w
$\rho_w(NH_2)+$	830 m	no	769 vw	914 vw	904 w	904 vw	906 w	894 w
$\rho_r(CH_2)$			no	no	858 w	853 w	no	no
$\rho_r(CH_2)$	–	no	no	no	822 w	823 vw	842 w	843 w
		738 w	no	no	no	no	no	no
δ(skeletal)	513 w	515 w	no	no	771 w	773 vw	789 vw	769 vw
	474 w	no	no	741 vw	737 w	737 w	736 w	735 w
	–	no	no	no	540 m,sh	540 m,sh	no	no
	–	no	no	no	458 m	no	no	no

[a,b,c]Takes from Refs. [16,7,15] respectively.

vs = very strong, s = strong, m = medium, vw = very weak, sh = shoulder, br = broad and no = not observed.

Table 2. The Vibrational Wavenumbers (cm^{-1}) of Cyanide Group for the dabn Clathrates*

Assignment[a]	$K_2Cd(CN)_4$[a]	$K_2Hg(CN)_4$[a]	Mn-en-Hg-2Bz[b]	Cd-en-Cd-2Bz[b]	Cd-en-Hg-2Bz[b]	Cd-dabn-Cd-Bz	Cd-dabn-Hg-Bz	Cd-dabn-Cd	Cd-dabn-Hg
ν_1(CN) A_1	(2149)	(2149)	(no)	(2170 vs)	(2175 vs)	(2176 vs)	(2175 vs)	(no)	(no)
ν_5(CN) F_2	2145	2146	2168 vs	2167 vs	2169 vs	2164 vs	2166 vs	2156 vs	2154 vs
	(no)	(no)	(no)	(2163 sh)	(2168 sh)	(no)	(no)	(no)	(no)
Hot band	no	no	no	2135 vw	no	2143 vw	2143 vw	(no)	2131 vw
ν_2(MC) A_1	(327)	(335)	(no)	(no)	(no)	(no)	(no)	(no)	(no)
$\nu_6[\nu(MC)+\delta(NCM)]$ F_2	316	330	356 s	354 s	355 s	361 s	360 s	355 s	353 s

vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder and no = not observed.
*The Raman bands are given in parentheses.
[a]Taken from Ref. [18].
[b]Taken from Ref. [7].

Table 3. The Vibrational Wavenumbers (cm^{-1}) of Benzene in the M-dabn-M′-Bz-Clathrates*

Assignment[a]	Liquid Benzene[b]	Mn-en-Hg-2Bz[c]	Cd-en-Cd-2Bz[c]	Cd-en-Hg-2Bz	Cd-dabn-Cd-Bz	Cd-dabn-Hg-Bz
$2\nu_8$	(3166)	(no)	(no)	(no)	(no)	(no)
ν_{20}, E_{1u}	3073	3082	3085 s	3086 m	3086 w	3085 w
$\nu_8+\nu_{19}$	3075	3062 m	3066 m	3064 m	3066 w	3066 w
ν_{13}, B_{1u}	3048	3029 s	3028 s	3032 s	3032 w	3032 w
ν_2, A_{1g}		3058 vw	3062 vw	3060 vw	no	no
	(3062 m)	(no)	(3060)	(3059 s)	(no)	(no)
ν_7, E_{2u}		3041 vw	3042 vw	3045 vw	no	no
	(3050 sh)	(no)	(3044 s)	(3044 s)	(no)	(no)
$\nu_5+\nu_{17}$, E_{1u}	1955	1960 w	1960 w	1964 w	1970 vw	1969 vw
ν_8, E_{2g}	(1586)	(no)	(1584 m)	(1584 m)	(no)	(no)
$\nu_{10}+\nu_{17}$	1815	1815 w	1818 w	1820 w	1828 w	1828 w
ν_{19}, E_{1u}	1479	1474 s	1477 s	1479 s	1473 s	1477 s
ν_{14}, B_{2u}	1309	no	1309 w	1310 w	1311 w	1311 w
ν_9, E_{2g}		1173 vw	1176 vw	1169 w	1177 vw	no
	(1177)	(no)	(1176 w)	(1175 w)	(no)	(no)
ν_{15}, B_{2u}	1149	1148 vw	1147 vw	1146 vw	1140 vw	1140 w
ν_{18}, E_{1u}	1036	1032 m	1033 m	1034 m	1034 m,sh	1035 m,sh
ν_1, A_{1g}	(991)	(no)	(992 vs)	(992 vs)	(991 vs)	(993 vs)
ν_5, B_{2g}	989	no	no	no	no	987 vw
ν_{17}, E_{2u}	966	no	no	no	974 vw	974 vw
ν_{10}, E_{1u}		848 vw	853 vw	849 vw	no	no
		(no)	(no)	(no)	(no)	(no)
ν_{11}, A_{2u}	670	688 sh	695 sh	700 sh	698 m,sh	700 s
		680 vs	683 vs	688 vs	685 s	687 s
		668 sh	676 sh	679 sh	679 w,sh	675 w,sh
ν_6, E_{2g}		603 vw	604 vw	601 vw	no	no
	(607)	(no)	(605 w)	(606 m)	(no)	(no)

*The Raman bands are given in parentheses.
[a]Taken from Ref. [24].
[b]Ir bands from Ref. [21], Raman bands from Ref. [22].
[c]Taken from Ref. [7].
v = very, s = strong, m = medium, w = weak, sh = shoulder and no = not observed.

as a chelation. A chelation arrangement have been noted for the residual host $Cd(en)Cd(CN)_4$ which is left after liberation of the guest benzene molecules from the en-bridged $Cd(en)Cd(CN)_4 \cdot 2C_6H_6$ clathrate.[17]

The vibrational data for $M(CN)_4$ groups in the compounds under study are given in Table 2, together with the vibrational wavenumbers of

$K_2Cd(CN)_4$ and $K_2Hg(CN)_4$.[18] The assigned wavenumbers for the $M(CN)_4$ groups in the compounds studied appear to be much higher then those for $M(CN)_4$ unit in $K_2M(CN)_4$ (M = Cd or Hg) (Table 2). Such frequency shifts have been observed for other T_d-type clathrates[6–8,10,11] and T_d-type complexes,[9,19] 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 Cd-NC vibrations.[6–13,19,20]

The assignment and the wavenumbers of the vibrational bands of the guest benzene molecule in the infrared and the Raman spectra of clathrate compounds studied are given in Table 3, together with some pertinent spectral data for comparison. The assignment and the wavenumbers of the vibrational bands of benzene observed in the infrared and Raman spectra of the clathrate compound studied are given in Table 3, along with the wavenumbers of benzene in the liquid phase[21] and in the clathrate Cd-en-Cd-2Bz[7] for comparison. The most structurally informative spectral features are the following.

Almost all of the vibrational bands (infrared and Raman) active bands of the isolated benzene molecule are observed in the infrared spectra of the clathrates (Table 3), suggesting that the selection rules for the benzene molecule under intrinsic (D_{6h}) are lost. This is possibly because of the low site symmetry of the benzene molecules in the clathrates.

The CH out-of-plane mode (A_{2u}) in the infrared spectra of the clathrates appears as a triplet (Table 3). This vibrational mode also appears as a doublet for Cd(pyrazine)$M(CN)_4 \cdot 2C_6H_6$ (M = Cd or Hg)[10] and $M(NH_3)_2M'(CN)_4 \cdot 2C_6H_6$ (M = Mn or Cd; M′ = Cd or Hg),[6] a triplet for M(ethylenediamine)$M'(CN)_4 2C_6H_6$ (M = Mn or Cd; M′ = Cd or Hg).[7] In the case of clathrates with doublet and triplet features, the splitting is explained by the strong host-guest interaction (i.e., crystal field effect).[10] 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.[11]

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 3). Similar positive shifts have been observed for Hofmann-type[22,23] and T_d-type clathrates.[6–8,10–13,20] This upward shift was explained for the Hofmann-type clathrates[22] by the presence of a weak hydrogen bond between π electrons located above and below the plane of the benzene ring and the ammonia of the lattice.

It should be noted that, in our clathrates, the number of guest molecules is 1,5. The decrease in the number of guest molecules from 2 in Hofmann-td-type[6–8] to 1,5 in the present series is due to the fact that the α-cavities may be occupied by the dabn molecules and the β-cavities may be occupy by the guest molecule.[15,16] A similar number has been found in Hofmann-diam-type clathrates.[14,15]

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