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Infrared Spectroscopic Study of T_d-Type Piperazinemetal(II) Tetracyanometallate(II) Benzene(1/1) Clathrates: $Cd(C_4H_{10}N_2)Cd(CN)_4 \cdot C_6H_6$ and $Cd(C_4H_{10}N_2)Hg(CN)_4 \cdot 1{,}25\ C_6H_6$

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Abstract: The title compounds have been prepared in powder form. Their spectral data have been compared with those of the corresponding host complexes and found to be consistent with the host structure found in T_d-type clathrates.

Keywords: Benzene, clathrates, inclusion compounds, infrared spectra, metal complexes, piperazine, tetracyanometallate

INTRODUCTION

Vibrational spectroscopy has long been recognized to be of value in revealing the structure of T_d-type clathrates[1–7] and T_d-type host complexes[8–11] that could be prepared in powder from. The host structure in these compounds, designated with a general formula $ML_xM'(CN)_4$ [M is a divalent metal atom, Mn, Zn,[6,11] or Cd,[1–11] M′ is a divalent metal atom, Zn,[6] Cd or Hg,[1–11] and $x = 1$ for bidentate and $x = 2$ for monodentate ligand, L, molecules], is formed from infinite $-M-L_X-M-L_X$ chains extending along the *a* and *b* axes alternately and the tetrahedral $M'(CN)_4^{2-}$ ions are arranged between the consecutive crossing $-M-L_X-M-L_X$ chains with the N-termini bound to the M atoms. [This structure may also be described as follows: In

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the host framework, the M′ atom is tetrahedrally coordinated to the carbon atoms of the four cyanide groups, while the M atom is octahedrally surrounded by six nitrogen atoms, two are from ligands attached to the Cd atom in positions *trans* to each other, the other four are from cyanide groups. The $M'(CN)_4^{2-}$ groups are linked by the CdLx moieties to form a three-dimensional network].[1–12] This structure provides two kinds of cavities, α and β, for the guest molecules. The α cavity has approximately the shape of a rectangular prism similar to those in Hofmann-type hosts, whereas the β cavity has the shape of a biprismatic cage, as shown in Fig. 1.[12,13]

In previous papers, Kantarcı and his research group reported vibrational spectral data for a number of T_d-type clathrates[1–7] and host complexes.[8–11] We have now prepared two similar new compounds $Cd(C_4H_{10}N_2)Cd(CN)_4 \cdot C_6H_6$ (abbr. Cd–pipz–Cd–Bz) and $Cd(C_4H_{10}N_2)Hg(CN)_4 \cdot 1{,}25\ C_6H_6$ (abbr. Cd–pipz–Hg–Bz) in powder form. In this study, we report the infrared and Raman spectra of these compounds. For the purposes of comparison and discussion, the corresponding host complexes, $Cd(C_4H_{10}N_2)Cd(CN)_4$ (abbr. Cd–pipz–Cd) and $Cd(C_4H_{10}N_2)Hg(CN)_4$ (abbr. Cd–pipz–Hg), have been prepared, and their spectral data are also reported. It should be noted that several unsuccessful attempts have been made to synthesize similar clathrates and host complexes with divalent Mn, Fe, Co, Cu, or Zn metal atoms in the octahedral arrangement.

EXPERIMENTAL

Preparations

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

The clathrates Cd–pipz–Cd–Bz and Cd–pipz–Hg–Bz were prepared by adding 1 mmol of piperazine and 1 mmol of $K_2M(CN)_4$ (M = Cd or Hg) solution in water to 1 mmol of $CdCL_2$ solution in water saturated with benzene. The precipitate was filtered, washed with water, ethanol, and

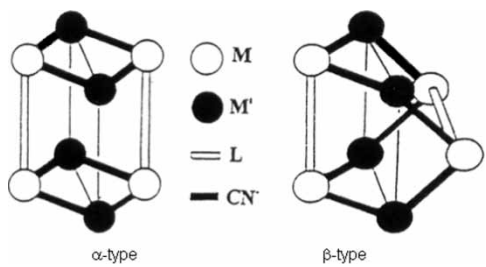

Figure 1. Two kinds cavities in the complexes.[13]

ether, successively, and kept in a desiccator containing saturated benzene vapor.

In the absence of benzene, the preparations given above result in the corresponding host complexes Cd–pipz–Cd and Cd–pipz–Hg.

The freshly prepared samples were analyzed for C, H, and N with the following results (found%/calculated%):

$$\begin{aligned}
Cd(C_4H_{10}N_2)Cd(CN)_4 \cdot C_6H_6\text{: } & C = 34.12/34.10, H = 3.48/3.27, N \\
& = 15.50/17.04 \\
Cd(C_4H_{10}N_2)Hg(CN)_4 \cdot 1,25C_6H_6\text{: } & C = 31.55/30.98, H = 2.92/2.93, N \\
& = 14.26/14.00 \\
Cd(C_4H_{10}N_2)Cd(CN)_4\text{: } & C = 24.22/23.15, H = 3.58/2.43, \\
& N = 20.12/20.25 \\
Cd(C_4H_{10}N_2)Hg(CN)_4\text{: } & C = 20.30/19.10, H = 3.43/2.00, \\
& N = 16.56/16.70
\end{aligned}$$

Spectra

Infrared spectra of the freshly prepared compounds were recorded between 4000 and 200 cm^{-1} on Perkin Elmer1330 and Mattson1000 FTIR spectrometers, which were calibrated using polystyrene and indene. The samples were prepared as mulls in Nujol and Fluorouble in a CsI cell and as KBr disks. Owing to the high-intensity fluorescense (with 488- or 514.5-nm line), we could only detect the strongest band of $Ni(CN)_4$ unit in the host complex $[\nu_1(A_1) = 2160\,cm^{-1}]$ using a Jobin-Yvon U1000 spectrometer and a spectra-Physics model 2016-4S argon ion laser. The spectrometer calibrated against the laser plasma emission lines.

RESULTS AND DISCUSSION

The compounds under study show no serious difference between the infrared spectra recorded in Nujol (or Fluorouble) mulls and KBr pellets.

The infrared spectra of Cd–pipz–Cd and Cd–pipz–Hg complexes are shown in Fig. 2. The vibrational spectral features of the compounds Cd–pipz–Cd–Bz and Cd–pipz–Hg–Bz and the complexes Cd–pipz–Cd and Cd–pipz–Hg are found to be very similar, suggesting that they have isomorphous crystal structures.

Because of the lack of structural data for the compounds studied, the vibrational assignment was made by treating the piperazine and benzene molecules and the $M(CN)_4^{2-}$ (M = Cd or Hg) ions as isolated units. The infrared wavenumbers and the assignments made are given for piperazine,

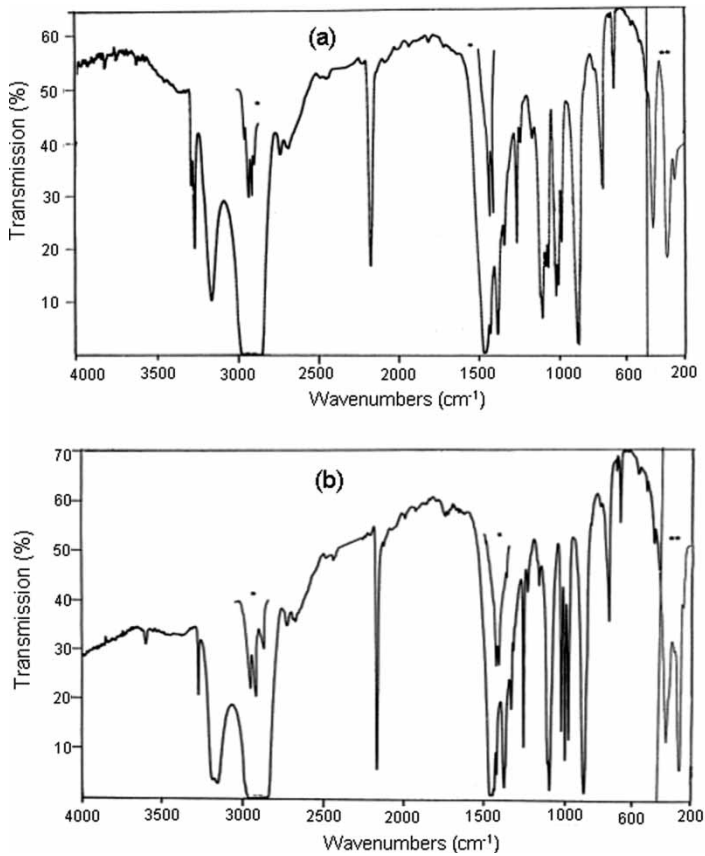

Figure 2. The Infrared spectra of Cd–pipz–Cd (a) and Cd–pipz–Hg (b) complexes in Nujol (*in poly-(chlortrifluorethylene)-oil, in Nujol between polyethylene windows).

benzene, and $M(CN)_4^{2-}$ units in Tables 1–3, respectively, along with same relevant spectral data for comparison.

Piperazine Vibrations

Few studies have been reported on the vibrational spectra of piperazine and coordinated piperazine in metal complexes. Of these, three reports are relevant to our purpose. From x-ray diffraction data, Hassel and Pedersen[14] have concluded that piperazine is centrosymmetric, having the chair conformation. Hendra and Powell[15] have assumed that the 1,4-dioxane molecule has a centrosymmetric chair conformation, at least in solution, and that the fundamental modes of 1,4-dioxane as illustrated by

Table 1. The vibrational wavenumbers (cm^{-1}) of piperazine in the Cd–pipz–M–Bz (M = Cd or Hg) clathrates

Assignment[a]	Piperazine (in CCl_4[a])	Piperazine (solid[a])	$HgCl_2 \cdot$ dioxane[b]	$Mn(dioxane)_2Hg(CN)_4$[c]	Cd–pipz–Cd	Cd–pipz–Hg	Cd–pipz–Cd–Bz	Cd–pipz–Hg–Bz
N–H str.	3276s	3225s	—	—	3194s	3188vs	3267vs	3261vs
CH_2 asymmetric str.	—	(3225s)	—	—	—	—	—	—
$\nu_{11}(a_u)$, $\nu_{28}(b_u)$ CH_2 str.	2945vs	2940s	—	—	2970s 2926s	2963s 2927s	2966s	2962s
CH_2 asymmetric str.	—	(2832s)	—	—	—	—	—	—
$\nu_{12}(a_u)$, $\nu_{29}(b_u)$ CH_2 str.	2825vs	2827vs	—	—	2876w,sh 2867s	2876w,sh 2857s	2862s	2862s
CH_2 scissor	—	(1455m)	—	—	—	—	—	—
$\nu_{30}(b_u)$ CH_2 scissor	1456s	1455s	—	1455s	1447s	1446s	1456s	1446s
$\nu_{13}(a_u)$ CH_2 scissor	1435sh	1446sh	—	—	1437s,sh	1435s	1439s	1435s
CH_2 scissor	—	(1446s)	—	—	—	—	—	—
$\nu_{31}(b_u)$ CH_2 wagging	1419sh	1414sh	—	—	1422s	1426s	1421s	1424s
CH_2 wagging	—	(1393w)	(1310w)	—	—	—	—	—
$\nu_{14}(a_u)$ CH_2 wagging	1398sh	1369m	—	1367w	1367w	1367w	1376s	1375s
$\nu_{32}(b_u)$ CH_2 twist	1319vs	1325m	1288m,s	1291m	1319w	1317w	1367w	1367w
CH_2 twist	—	(1297vs)	(1220w)	—	—	—	—	—
$\nu_{15}(a_u)$ CH_2 twist	1265s	1266s	1253s	1256s	1255s	1255vs	1255s	1255s
CH_2 twist	—	(1184vs)	—	—	—	—	—	—
$\nu_{16}(a_u)$	1136vs	1132vs	1125sh 1111s 1102sh	1118s	1145w	1148w	1156w	1158w
Ring str.	—	(1123m)	(1132w)	—	—	—	—	—
Ring str.	—	(1119s)	(1094vw)	—	—	—	—	—
$\nu_{17}(a_u)$ CH_2 rock	1072m	1084m	1081m,s	1084s	1097vs	1095vs	1097vs	1095vs

(*continued*)

Table 1. Continued

Assignment[a]	Piperazine (in CCl_4[a])	Piperazine (solid[a])	$HgCl_2 \cdot$ dioxane[b]	$Mn(dioxane)_2$ $Hg(CN)_4$[c]	Cd–pipz–Cd	Cd–pipz–Hg	Cd–pipz–Cd–Bz	Cd–pipz–Hg–Bz
CH_2 rock	—	(1109vs)	(1018m,w)	—	—	—	—	—
$\nu_{33}(b_u)$ ring str.	1055m	1000m	1038m,s	1046m	1020s 999s	1018s 997s	1020s	1018s
$\nu_{34}(b_u)$ CH_2 wagging	930m	962m	890m,s	894s	978s	978s	999s	997s
CH_2 rock	—	(866vs)	(856w)	—	—	—	—	—
Ring str.	—	(836vs)	(827m)	—	—	—	—	—
$\nu_{18}(a_u)$ ring str.	849s	833s	855s	856vs	881vs	879vs	881s	879s
$\nu_{35}(b_u)$ ring band	567vs	616s 591s	616s	615s	648w	644w	648w	644w
Ring band	—	(481w)	—	—	—	—	—	—
Ring band	—	(448vw)	(456w)	—	—	—	—	—
Ring band	—	(404vw)	—	—	—	—	—	—
$\nu_{19}(a_u)$ ring band	—	317s	—	—	346s	319s	323s	319s
$\nu_{36}(b_u)$ ring band	—	272vs	—	—	261s	245s	248s	272vs

Raman bands are in parentheses. v, very; s, strong; m, medium; w, weak; sh, shoulder; str., stretching.

[a]Taken from Ref.[15]

[b]Taken from Ref.[19]

[c]Taken from Ref.[20]

Table 2. The vibrational wavenumbers (cm^{-1}) of the $M(CN)_4^{2-}$ group for the Cd–pipz–M (M = Cd or Hg) complexes and Cd–pipz–M–Bz (M = Cd or Hg) clathrates

Assignment[a]	$K_2Cd(CN)_4$[a]	$K_2Hg(CN)_4$[a]	Cd–pipz–Cd	Cd–pipz–Hg	Cd–pipz–Cd Bz	Cd–pipz–Hg Bz
ν_1(CN) A_1	(2149)	(2149)	nm	nm	(2173vs)	(2174vs)
ν_5(CN) F_2	2145	2146	2168vs	2168vs	2171vs	2170vs
ν_2(MC) A_1	(327)	(335)	nm	nm	nm	nm
Hot band	nm	nm	nm	nm	nm	nm
$\nu_6[\nu(MC),\delta(NCM)]$ F_2	316	330	362	369	353s	350s
$\nu_7[\nu(MC),\delta(NCM)]$ F_2	250	235	260	259	261m	248m

Raman bands are in parentheses. nm, not measured; v, very; s, strong; m, medium.
[a]Taken from Ref.[23]

Table 3. The wavenumbers frequencies of benzene in the clathrates (cm^{-1})

Assignment[a]	Benzene Liquid[b]	Cd–en–Cd 2Bz[c]	Cd–en–Hg 2Bz[c]	Cd–pipz–Cd Bz	Cd–pipz–Hg Bz
$2\nu_8$	(3166)	nm	nm	nm	nm
ν_{20}, E_{1u}	3073	3085s	3086s	3088m	3088m
$\nu_8 + \nu_{19}$	3075	3066m	3064m	nm	nm
ν_{13},B_{1u}	3048	3028m	3032m	3068m	3068m
ν_2, A_{1g}	(3062m)	(3060s)	(3059s)	nm	nm
ν_7, E_{2g}	(3050sh)	(3044s)	(3044s)	nm	nm
$\nu_5 + \nu_{17}$, E_{1u}	1955	1960w	1964w	1961w	1961w
ν_8, E_{2g}	(1586m)	(1584m)	(1585m)	nm	nm
$\nu_{10} + \nu_{17}$	1815	1818w	1820w	1817w	1819w
ν_{19},E_{1u}	1479	1477s	1479s	1477w	1475m
ν_{14},B_{2u}	1309	1309w	1310w	nm	1313vw
ν_9, E_{2g}	(1177m)	(1176w)	(1175w)	nm	nm
ν_{15},B_{2u}	1149	1147vw	1146vw	1145w,sh	1145w,sh
ν_{18},E_{1u}	1036	1033m	1034m	1036sh	1036sh
ν_1, A_{1g}	(991vs)	(992vs)	(992vs)	nm	nm
ν_{17},E_{2u}	966	nm	nm	nm	978sh
ν_{10}, E_{1u}	(850)	nm	nm	nm	nm
ν_{11},A_{2u}	670	695sh	700sh	685vs	683vs
		683vs	688vs		
		676sh	679sh		
ν_6, E_{2g}	(607)	(605m)	(606m)	nm	nm

Raman bands are in parentheses. v, very, s, strong, m, medium, w, weak, sh, sholuder, nm, not measured.
[a]Taken from Ref.[27]
[b]Taken from Ref.[28]
[c]Taken from Ref.[4]

Ramsey[16] could be assumed to apply to piperazine. They have also studied the infrared spectra of the 1:2 complex with $C_2H_4PtCL_2$ and have shown that this complex contains a piperazine molecule in a chair conformation, bridging to acceptor molecules.[17]

In assigning the spectral bands of free piperazine, we adopted the method of Hendra and Powell[15]; that is, the fundamental modes of 1,4-dioxane could be assumed to apply to piperazine. As doing this, we refered to the complete vibrational assignments for 1,4-dioxane presented by Ellestad et al.[18]

The assignments and the wavenumbers of the fundamental bands assignable to the piperazine molecule in solution in CCl_4 and in the solid phase and in the compounds under study are given in Table 1. For the sake of comparison, Table 1 also reports the infrared spectra of $HgCL_2 \cdot$ dioxane[19] and $Mn(dioxane)_2Hg(CN)_4$ complexes (abbr. Mn–diox–Hg).[20] The crystal structure[21] and the vibrational spectral studies[19] of the former complex show it to be centrosymmetric with bridging dioxane molecules in the chair conformation. The spectral data of the latter compound is consistent with the T_d-type framework.[20]

The spectral data for piperazine in the complexes and clathrates exhibit characteristics of a coordinated ligand (Table 1); that is, on coordination, the N–H stretching frequencies should decrease, while the C–H stretching frequencies should increase due to the consecutive inductive effects (on coordination, N–H and N–C bonds should become weaker and C–H bonds should become stronger).[22] These requirements are fulfilled for piperazine in our compounds (Table 1). From a comparison of the spectral data presented in Table 1, we conclude that the coordinated piperazine molecules in the compounds studied are present in the bridging "chair" conformation. This conclusion is based on the apparent absence of any inactive band in the infrared and Raman spectra of piperazine molecule in the clatrate compounds (Table 1).

$M(CN)_4$ (M = Cd or Hg) Group Vibrations

In assigning the bands attributable to the $M(CN)_4$ group in the spectra of our compounds, it is appropriate to refer to the work of Jones, who presented vibrational data for the salts $K_2Cd(CN)_4$ and $K_2Hg(CN)_4$ in the solid phase.[23] Structural studies have shown that the K-NC distance is ca. 2.9 Å in $K_2Cd(CN)_4$[24] and $K_2Hg(CN)_4$,[25] while the Cd-NC distance is ca. 2.3 Å in T_d-type host frameworks.[26] Therefore, they can be used as references to account for the spectral changes when the stiffer Cd-NC bonding takes place. The spectral data for $M(CN)_4$ groups in the clathrate are given in Table 2, together with the infrared data of the $K_2Cd(CN)_4$ and $K_2Hg(CN)_4$ salts.[23] The wavenumbers assigned for the $M(CN)_4$ group in the compounds studied appear to be much higher than those for the $M(CN)_4$ ions in $K_2M(CN)_4$ (Table 2). Such frequency shifts have been observed for

other T_d-type clathrates, 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 Cd-NC vibrations.[1–11] It follows that the N-ends of the $M(CN)_4$ groups are also bound to an Cd atom in our clathrates compounds.

Benzene Vibrations

The assignments and the wavenumbers of the infrared bands of benzene observed in the infrared spectra of the clathrate compounds studied are given in Table 3, along with the frequency of benzene in the liquid phase[28] and benzene in Cd(ethylenediamine)$M(CN)_4$ 2Bz (M = Cd or Hg) clathrates,[5] on which the assignments are based. The most structurally informative spectral features are as follows.

All of the vibrational 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 its intrinsic symmetry (D_{6h}) are lost. This is possibly due to the low site symmetry of the guest molecules in the clathrate.

The CH out-of-plane mode (A_{2u}) in the infrared spectra of the clathrates appears as a very intense single band at 685 cm^{-1} in the infrared spectra of the clathrate compounds (Table 3). A similar single band was also observed in the infrared spectra of the Hofmann-type clathrates $M(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ (M = Mn, Fe, Ni, Cu, Zn, or Cd)[29] and T_d-type clathrates Cd(4,4′-bipyridyl)$M(CN)_4 \cdot 2C_6H_6$ (M = Cd or Hg).[2] This vibrational mode splits into a doublet for Cd(pyrazine)$M(CN)_4 \cdot 2C_6H_6$ (M = Cd or Hg)[1] and M(trimethylenediamine) $Zn(CN)_4 \cdot 2C_6H_6$ (M = Mn or Zn)[6] and into a triplet for M(ethylenediamine)$M'(CN)_4 \cdot 2C_6H_6$ (M = Mn or Cd, M′ = Cd or Hg).[4] In the case of clathrates with doublet and triplet features, the splitting is explained by the strong host–guest interactions (i.e., crystal field effects).[1–6] In the case of clathrates with a single band, because of the larger cavities due to the ligands or because of the flexibility of the ligand such as piperazine in the current clathrates, the host–guest interactions are expected not to be effective for splitting.[1–6]

Another feature of the CH out-of-plane (A_{2u}) 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[29] and T_d-type[1–6] 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 piperazine ligand molecules of the host lattice, as has been suggested for other clathrates.[1–6,29] Therefore, we reasonably suggest that the frequency shifts in our clathrates are due to the π electrons donation from the benzene ring to the hydrogen atoms of the NH groups in the piperazine, which have a more electrophilic character caused by the bidentate coordination.

The preceding discussion considered as a whole leads us to the conclusion that the host lattice of our clathrates is similar to those of T_d-type clathrates.

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