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An Infrared and Raman Spectroscopic Study of Pyrazinecadmium (II) Tetracyanometalate (II) Benzene (1/1) Clathrates: $Cd(C_4H_4N_2)Cd(CN)_4{\cdot}C_6H_6$ and $Cd(C_4H_4N_2)Hg(CN)_4{\cdot}C_6H_6$

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Abstract. Two new benzene clathrates of the form $Cd(Pyrazine)M(CN)_4{\cdot}C_6H_6$, where M = Cd or Hg, have been prepared and their infrared and Raman spectra are reported.

Key words. Hofmann-Td-type benzene clathrate, Cd–pyrazine complex, benzene inclusion compound, IR and Raman spectra.

1. Introduction

It has been shown that the host frameworks of the Hofmann-Td-type clathrates appear to be excellent reservoirs for thermally unstable radicals such as the cyclohexadienyl, $C_6H_7^{\cdot}$, radical [1, 2]. These compounds are formulated as $Cd(II)L_2M(II)(CN)_4{\cdot}nG$, where L_2 is a bidentate ligand or a pair of unidentate ligand molecules, M is Cd or Hg and n is the number of G (guest) molecules depending on the bulkiness of the ligands. The host framework is formed from endless chains of —Cd—L_2—Cd— extending along the a and b axes alternately and the tetrahedral $M(CN)_4$ ions arranged between the consecutive crossing —Cd—L_2—Cd— chains with the N-ends bound to the Cd atoms [3–6]. 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 Hofmann-type hosts, while the β cavity is a twisted biprism, as has been demonstrated in previous papers [3–6]. The clathrate compounds possessing the Td-type of host lattice reported to date have been formed with the following ligands: ammonia, ethylenediamine, trimethylenediamine and propylenediamine [5, 7].

In our previous work we have reported the vibrational spectroscopic results of $M'(pyz)Ni(CN)_4{\cdot}n\ C_6H_6$ clathrates (where M′ = Ni or Cd, pyz = pyrazine, n = 0–0.5) [8], which are obtained by replacing the two NH_3 molecules between adjacent square planar tetracyanonickelate sheets in the Hofmann type clathrates, $M'(NH_3)_2Ni(CN)_4{\cdot}2\ C_6H_6$, by a bidentate pyrazine ligand, in which the sheets are

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spread out in the form of a three-dimensional host structure. Now we have prepared pyrazinecadmium (II) tetracyanometalate (II) benzene (1/1), Cd(pyz) $M(CN)_4 \cdot C_6H_6$ (M = Cd or Hg, abbreviated to Cd-M-pyz-B), for the first time, using tetrahedral $Cd(CN)_4$ or $Hg(CN)_4$ ions instead of square planar $Ni(CN)_4$, with the aim of giving further examples of Td-type clathrates. In this study the IR and Raman spectroscopic results of Cd-Cd-pyz-B and Cd-Hg-pyz-B are reported.

2. Experimental

2.1. PREPARATIONS

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

2.1.1. *Cd-Cd-pyz-B*

The colourless crystals were prepared by a diffusion method in a U-tube as follows: a mixture of benzene and chloroform (1 : 20 v/v) was put into a U-tube to a depth of about two thirds of its height. One limb of the U-tube was filled with a solution of $Cd(CN)_2$ (2 mmol) in water (10 mL) saturated in benzene. The other limb was filled with a solution of pyrazine (1 mmol) in benzene (10 mL). The whole system of three phases was allowed to stand at room temperature for three weeks. Needle-like colourless crystals grown at the interface between the aqueous and organic phases were removed and washed on a sintered glass filter with a benzene solution of water and kept in a desiccator containing molecular sieve and a saturated benzene atmosphere.

2.1.2. *Cd-Hg-pyz-B*

The preparation of this clathrate was similar to the previous one using a solution of $Cd(CN)_2$ (1 mmol) and $Hg(CN)_2$ (1 mmol) in place of $Cd(CN)_2$ (2 mmol).

2.1.3. *Analytical Results*

The freshly prepared samples were analysed for metal content by an X-ray fluorescence method on a GE SPG-7 XRF spectrometer, with the results as follows (%): Calculated for $Cd(C_4H_4N_2)Cd(CN)_4 \cdot C_6H_6$: Cd, 46.16. Found: Cd, 46.20. Calculated for $Cd(C_4H_4N_2)Hg(CN)_4 \cdot C_6H_6$: Cd, 19.54; Hg, 34.88. Found: Cd, 19.60; Hg, 34.90.

2.2. SPECTRA

Infrared spectra of the compounds were recorded between 4000 and 300 cm^{-1} on Perkin Elmer 1330 and Nicolet MX-IE spectrometers which were calibrated using polystyrene and CO_2 bands. The samples were prepared as mulls in nujol and hexachlorobutadiene between CsI plates.

The Raman spectra of the samples were excited using the 488.0 nm line of an Ar ion laser and recorded on a Cary 81 spectrometer with a slit width of 3.2 cm^{-1} by use of a spinning cell.

3. Results and Discussion

The IR spectra of the Cd-Cd-pyz-B and Cd-Hg-pyz-B clathrates are given in Figures 1a and b, respectively. The Raman spectrum of the Cd-Cd-pyz-B clathrate is given in Figure 2. The infrared and Raman spectral features of the two clathrates are found to be very similar, suggesting that they have isomorphous crystal structures. Owing to the lack of structural data the assignment was made by treating the pyrazine and benzene molecules and the $M(CN)_4^{2-}$ ($M = Cd$ or Hg) ions as isolated units. The vibrational wavenumbers of the bands in the IR and Raman spectra of the compounds studied are tabulated in Tables I–III together with some relevant spectral data for comparison. It should be noted that for the purposes of comparison and discussion several unsuccessful attempts have been made to obtain host complexes of the form $Cd(pyz)M(CN)_4$ ($M = Cd$ or Hg), without using benzene. These host complexes cannot be obtained by decomposition of the clathrates, since it has been found that the liberation of the benzene guest molecules is accompanied by the liberation of the pyrazine ligands. For example the IR spectrum of the Cd-Hg-pyz-B clathrate, after being heated at 90°C for one hour under reduced pressure (1 Pascal), shows that 70% of the benzene molecules escape but the intensity of the pyrazine bands are also found to decrease by approximately 70% in comparison with those of the fresh sample. The ν (CN) band is also found to be shifted to a higher wavenumber and to be broadened, indicating the breakage of Cd—pyrazine bonds and the liberation of the pyrazine molecules.

3.1. PYRAZINE VIBRATIONS

Evidence that the molecule of pyrazine, ($C_4H_4N_2$) has the centro symmetric and planar structure with the symmetry D_{2h} in the vapour and solid phases has been provided by electron diffraction [9, 10] and X-ray diffraction [11, 12] studies, respectively. The assignments of the infrared and Raman spectra of pyrazine in the solid [13], liquid [14, 15] and vapour [16, 17] phases and in solution [13, 17] have been reported to be in accord with the D_{2h} symmetry. In metal complexes in which both nitrogen atoms of pyrazine are coordinated to two identical metal atoms, the D_{2h} symmetry is preserved but is removed in unidentate coordination [18, 21].

The assignments and the wavenumbers of the vibrational bands of the pyrazine observed in the IR and Raman spectra of the Cd-Cd-pyz-B and Cd-Hg-pyz-B clathrates are given in Table I, together with the wavenumbers of pyrazine in solution [17, 13] on which the assignments are based. The pyrazine wavenumbers observed in the vibrational spectra of $SnCl_4pyz$ [18] and $CoCl_2pyz_2$ [19], which are known to be pyrazine bridged complexes on the basis of spectral [18] and crystallographic [22] studies, respectively, and of the $Cd(pyz)Ni(CN)_4 \cdot 0.5\,C_6H_6$ clathrate, which is assumed to have pyrazine bridges [8] on the basis of mid-IR and Raman spectra, are included for comparison.

The vibrational wavenumbers of the pyrazine modes of the Cd-M-pyz-B clathrates exhibit coordination properties, i.e., several modes of pyrazine have upward shifts in frequency in comparison with those of pyrazine in solution [17, 13]. The vibrational wavenumbers of Cd-Cd-pyz-B and Cd-Hg-pyz-B are found to be very similar, indicating that the pyrazine wavenumber values are not affected

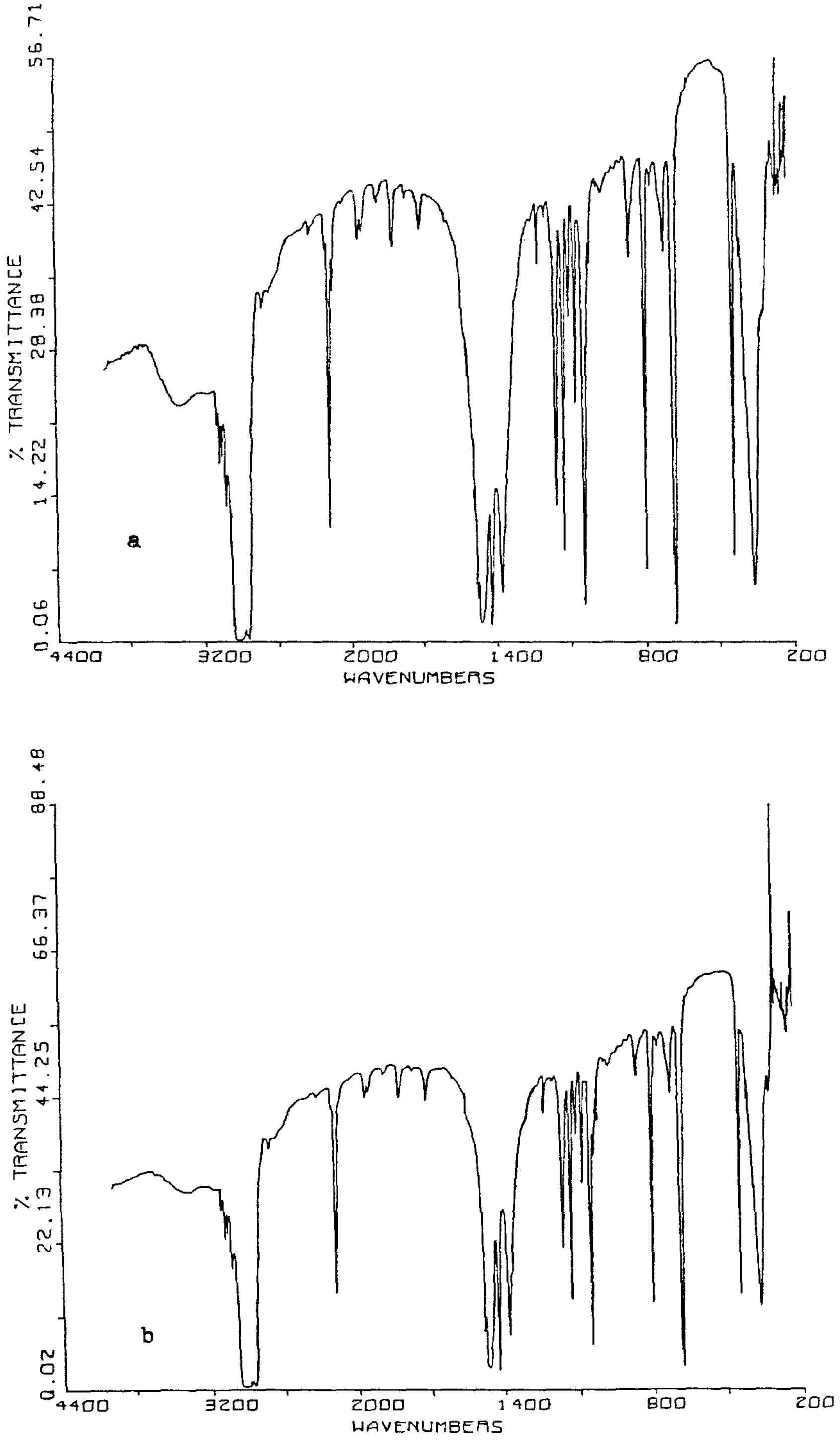

Fig. 1. The IR spectra of the Cd-Cd-pyz-B (a) and Cd-Hg-pyz-B (b) clathrates.

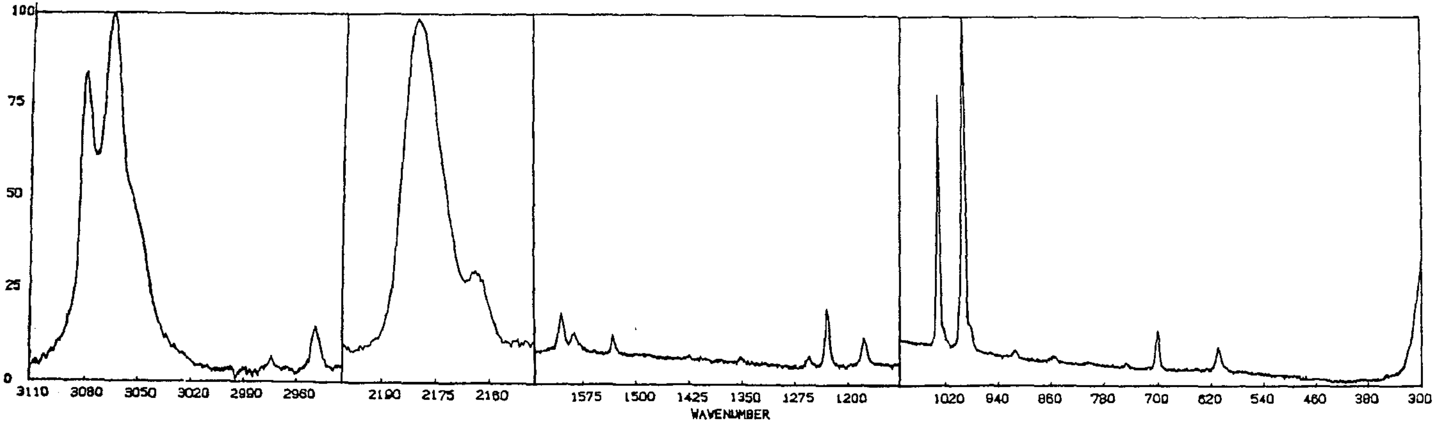

Fig. 2. The Raman spectrum of the Cd-Cd-pyz-B clathrate.

Table 1. Vibrational wavenumbers (cm^{-1}) of pyrazine in Cd-M-pyz-B and related compounds.

Symmetry and assignment[a]	Pyrazine solution		$SnCl_4pyz$[c]		$CoCl_2pyz_2$[d]		Cd-Ni-pyz-B[e]		Cd-Cd-pyz-B		Cd-Hg-pyz-B	
	IR[a]	Ra[b]	IR	Ra	IR	Ra	IR	Ra	IR	Ra	IR	Ra
16b;B_{2u} γ_{ring}	418	–	473	–	470	–	451	–	448vs	–	448vs	–
6b;B_{2g} δ_{ring}	–	701	–	701	–	700	–	702	–	699w	–	700w
4;B_{3g} γ_{ring}	–	756[f]	–	728	–	750	–	748	–	748vw	–	747vw
11;B_{2u} γ(CH)	785	–	790 798	–	810 815	–	796	–	801vs	–	801vs	–
10a;B_{1g} γ(CH)	–	919	–	864	–	918	–	913	–	914vw	–	913vw
5;B_{3g} γ(CH)	–	983[f]	–	–	–	–	–	–	–	982wsh	–	982wsh
1;A_g ν_{ring}	–	1011	–	1020	–	1032	–	1027	–	1028vs	–	1028vs
12;B_{1u} δ_{ring}	1019	–	1070	–	1050	–	1047	–	1048vs	–	1048vs	–
15;B_{3u} δ_{CH}	1061	–	–	–	–	–	1078	–	1079m	–	1080m	–
18a;B_{1u} δ(CH)	1130	–	1120	–	1110	–	1125	–	1128 1125sp	–	1128s	–
14;B_{3u} ν_{ring}	1150	–	1180	–	1150	–	1157	–	1158s	–	1158s	–
9a;A_g δ(CH)	–	1231	–	1224	–	1214	–	1230	–	1230m	–	1229m
3;B_{2g} δ(CH)	–	1343	–	–	–	–	–	1370	–	1352vw	–	1351vw
19b;B_{3u} ν_{ring}	1412	–	1430	–	1405	–	1419	–	1422s	–	1422s	–
19a;B_{1u} ν_{ring}	1483	–	–	–	1480	–	1481	–	1490w	–	1490w	–
8b;B_{2g} ν_{ring}	–	1524	–	1528	–	1524	–	1522	–	1531w	–	1531w
8a;A_g ν_{ring}	–	1574	–	1624	–	1604	–	1587	–	1586w	–	1586w
13;B_{1u} ν(CH)	3011	–	3080	–	3080	–	3043	–	–	3034s	–	3034s
7b;B_{2g} ν(CH)	–	3040	–	–	–	–	–	–	–	3053sh[g]	–	nm
2;A_g ν(CH)	–	3054	–	3108	–	3092	–	3078	–	3078s	–	nm
20b;B_{3u} ν(CH)	3061	–	3120 3140	–	3100	–	3095	–	3119m	–	3110m	–

[a,b,c,d] Taken from Refs. [17, 13, 18, and 19], respectively. [e] $Cd(pyz)Ni(CN)_4 \cdot 0.5\ C_6H_6$ wavenumbers are taken from ref. [8]. [f] liquid phase value. [g] Overlapped with benzene band, vs = very strong, s = strong, w = weak, vw = very weak, sh = shoulder, sp = split, nm = not measured.

by the slight changes in unit cell dimensions, if the metal M′, (here M′ = Cd) to which pyrazine is attached is the same. It must be noted that in the case of M′(pyz)Ni(CN)$_4$·*n* C_6H_6 compounds pyrazine wavenumbers are found to be greatly altered by changing the metal (M′) from Cd to Ni, which was explained as the coupling of the internal modes of pyrazine with the M′—N(pyrazine) vibrations [8].

The most significant vibrational spectral difference observed for the pyrazine complexes containing bidentate bridging pyrazine compared with compounds containing the unidentate terminal ligand is the absence of coincidence between IR and Raman bands. This fact is clearly shown in the vibrational spectroscopic study on pyrazine halide complexes [18, 19] and also in our previous study on pyrazinecadmium (II) tetracyanonickelate compounds, Cd(pyz)Ni(CN)$_4$·*n* C_6H_6 and Cd (pyz)$_2$Ni(CN)$_4$, which contain bidentate bridging and unidentate terminal pyrazine ligands, respectively [8].

It is clear from Table I that the lack of coincidences between infrared and Raman wavenumbers implies the bidentate coordination of pyrazine in the Cd-M-pyz-B clathrates.

3.2. BENZENE VIBRATIONS

The vibrational wavenumbers of the benzene bands in the IR and Raman spectra of the clathrates studied are tabulated in Table II. The most outstanding vibrational feature which merits comment is the following: The A_{2u} CH out-of-plane vibration gives a doublet appearing at 685 and 681 cm^{-1}. This vibrational band is observed as triplets in the IR spectra of both Hofmann-Td-type, Cd(NH$_3$)$_2$M(CN)$_4$·2 C_6H_6 [23] and en-Td-type, Cd(en)M(CN)$_4$·2 C_6H_6 (where en = ethylenediamine, M = Cd or Hg) [4], clathrates. The X-ray diffraction analyses of these compounds [3, 6] have shown the presence of two kinds of cavities (α and β) containing the guest benzene molecules. In the case of Hofmann-Td-type clathrates, since the benzene molecules of the two α-cavities are found to be in different orientations, three crystallographically independent benzene molecules are present [3]. But in the case of en-Td-type clathrates the benzene centers of the two α-cavities are found to be crystallographically equivalent to each other [6]. On the other hand there is no reported crystallographic study on Cd-M-pyz-B clathrates, therefore their structures, and thus the orientation of the guest benzene molecules are unknown. However, based on the vibrational spectroscopic results, we propose that they have a very similar structure to that of the en-Td-type clathrate, Cd(en)M(CN)$_4$·2 C_6H_6 [4] with the bridging pyrazine ligand analogous to en. But it must be pointed out that in spite of our efforts to trap more benzene molecules in the host structure of the present series, we have only obtained the composition Cd(pyz)M(CN)$_4$·C_6H_6. The decrease of *n* from 2 in en-Td-type and in Hofmann-Td-type clathrates to 1 in the present series may be explained by the fact that the pyrazine ligand is bulkier than an ethylenediamine or a pair of ammonia molecules, therefore one of the cavities, most probably α, may be occupied by a pyrazine ligand and so only the other cavity, β, may be effective in accomodating the guest benzene molecule. Hence the doublet structure of the $\gamma(CH)A_{2u}$ mode of benzene may not arise due to the occupation of both α and β cavities but may be due to the crystal field effect. A complete single crystal study is required to shed light on these arguments.

Table II. Vibrational wavenumbers (cm^{-1}) of benzene in Cd-Cd-pyz-B, Cd-Hg-pyz-B and in other host frameworks.

Assignment[a]	Liquid benzene		Cd-Ni-NH$_3$-B[b]		Cd-Hg-NH$_3$-B[c]	Cd-Cd-pyz-B		Cd-Hg-pyz-B	
	IR[d]	Ra[e]	IR[f]	Ra[e]	IR[g]	IR	Ra	IR	Ra
$\nu_8 + (\nu_1 + \nu_6)$	–	3187	–	3180	–	–	3183vw	–	nm
$2\nu_8$	–	3166	–	3160	–	–	3163vm	–	nm
$\nu_{20} E_{1u}$	3073	–	3076	–	3076	3088s	–	3088s	–
$\nu_{13} B_{1u}$	3062[h]	–	3026	–	3056	3068m	–	3068m	–
$\nu_2 A_{1g}$	–	3062	–	3064	–	–	3062m	–	3062m
$\nu_7 E_{2g}$	–	3050	–	3049	–	–	3053sh	–	3053sh
$\nu_3 + \nu_1 + \nu_6$	–	2949	–	2943	–	–	2950w	–	2950w
$(\nu_5 + \nu_{17}) E_{1u}$	1955	–	–	–	1955	1951w	–	1951w	–
$\nu_1 + \nu_6$ } in resonance	–	1606	–	1601	–	–	1603m	–	1604m
$\nu_8 E_{2g}$	–	1586	–	1583	–	–	1586[i]m	–	1586[i]m
$\nu_{19} E_{1u}$	1479	–	1476	–	1480	1479m	–	1479m	–
$\nu_{14} B_{2u}$	1309	–	1311	–	–	–	–	–	–
$\nu_9 E_{2g}$	–	1177	–	1178 1170	–	–	1177w	–	1177m
$\nu_{15} B_{2u}$	1149	–	1147	–	–	1147sh	–	1147sh	–
$\nu_{18} E_{1u}$	1036	–	1034	–	1035	1035m	–	1035m	–
$\nu_1 A_{1g}$	–	991	–	991	–	–	991vs	–	991vs
$\nu_1 (^{13}C^{12}C_5H_6)$	–	983	–	982	–	–	982w	–	982w
$\nu_{17} E_{2u}$	966	–	985	–	–	–	975vw	–	975vw
$\nu_{10} E_{1g}$	–	850	–	869	–	–	855w	–	854vw
$\nu_{11} A_{2u}$	670	–	704	–	701 688 676	685 681 vs	–	685 681 vs	–
$\nu_6 E_{2g}$	–	607	–	608	–	–	608	–	608
$\nu_{16} E_{2u}$	404	–	–	–	–	–	–	–	–

[a] Using the numbering system of E. B. Wilson, *Phys. Rev.* **45**, 706 (1934). [b] Cd(NH$_3$)$_2$Ni(CN)$_4$·2 C$_6$H$_6$. [c] Cd(NH$_3$)$_2$Hg(CN)$_4$·2 C$_6$H$_6$. [d,e,f,g] Taken from refs. [24, 25, 26 and 23], respectively. [h] Calculated value. [i] Overlapped with pyrazine band. nm = not measured.

Table III. Cyanide group vibrational wavenumbers (cm^{-1}) for Cd-Cd-pyz-B and Cd-Hg-pyz-B.

Symmetry and assignment[a]	$K_2Cd(CN)_4$[a]		$K_2Hg(CN)_4$[a]		Cd-Cd-pyz-B		Cd-Hg-pyz-B	
	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	2162w	2165vw	2162w
$\nu(^{13}CN)$	–	–	–	–	2142w	–	–	–
$\nu_2(MC)A_1$	–	327	–	335	–	354vw	–	–
$\nu_6[\nu(MC) + \delta(NCM)]F_2$	316	–	330	–	365vs	–	368vs	–

[a] Taken from ref. [27].

3.3. Cd(CN)$_4$ AND Hg(CN)$_4$ GROUP VIBRATIONS

In the Hofmann-Td-type clathrates studied previously [5] the metal atom M in $M(CN)_4$ is tetrahedrally surrounded by the carbon ends of four CN ions. Therefore, it is reasonable to assume that the clathrates studied here also have tetrahedral $M(CN)_4$ moities. In interpreting the bands attributable to the $M(CN)_4$ (M = Cd or Hg) ion in the spectra of our complexes, we 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 state [27]. In these salts the anions $[M(CN)_4]^{2-}$ are not coordinated to the K^+ ion, therefore they can be treated as isolated units and thus used as the references to comment on vibrational changes when M—NC coordination takes place. The vibrational data for $M(CN)_4$ groups in the clathrates studied are given in Table III, together with the vibrational wavenumbers of $K_2Cd(CN)_4$ and $K_2Hg(CN)_4$. The assigned wavenumbers of the $M(CN)_4$ group of the clathrates appear to be much higher than those for isolated $M(CN)_4$ units (Table III). Such frequency shifts have been observed for Hofmann type tetracyanonickelate compounds, in which both ends of the CN group are coordinated and explained as the mechanical coupling of the internal modes of $Ni(CN)_4$ with the metal (Cd)-NC vibrations (28). It follows that the N-ends of the $M(CN)_4$ units are also bound to a Cd atom in the clathrates $Cd(pyz)M(CN)_4 \cdot C_6H_6$.

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