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INFRARED SPECTRA OF HOFMANN-T_d-TYPE HOST COMPLEXES: $Cd(PYRIDINE)_2$ $Cd(CN)_4$ AND $Cd(PYRIDINE)_2$ $Hg(CN)_4$

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ABSTRACT

Two new Hofmann- T_d -type camplexes of the form Cd (11) $(Pyridine)_2$ M(11) $(CN)_4$ (M= Cd or Hg) have been prepared and their infrared spectra are reported. Spectral data indicate that the structure of the complexes consists of host framework formed from tetrahedral $M(CN)_4$ ions bridged by $Cd(Pyridine)_2$ cations so that the Cd is octahedrally surrounded by six N atoms, four from CN groups in a plane and two from the pyridine molecules.

INTRODUCTION

Among the Hofmann type and the analogous host lattices, a group of complexes designated with a general formula $CdL_2M(CN)_4$, where, L_2 is a bidentate or a pair of monodentate ligand molecules containing N-donor atoms and M is Cd or Hg, is of special interest, since their hosts act as excellent reservoirs for the thermally unstable chemical species such as cyclohexadienyl, C_6H_7., radicals [Iwamoto et al., 1978]. In these compounds the host framework is formed from infinite $-Cd-L_2-Cd-L_2$ chains extending along a– and– b–axes alternately and the tetrahedral $M(CN)_4$ ions arranged between the consecutive crossing $-Cd-L_2-Cd-L_2$ chains with the N – ends bound to the Cd atoms [Iwamoto, 1981]. This structure provides two kinds of cavities, α and β, for the quest molecules. The α cavity has approximately the shape of a rectangular prism, while the β cavityhas the shape of a biprism. The compounds possessing this type of host frameworks reported to date have been with the following ligands: ammonia [Iwamoto and Shrıver, 1972], ethylenediamine [Iwamoto, 1973; Kurada, 1973], trimethylenediamine [Iwamoto et al., 1978]. and propylenediamine [Nishikiori

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et al., 1980]. In order to increase the number of host complexes in this group of compounds, we have prepared two new py(pyridine) complexes: $Cd(py)_2Cd(CN)_4$ and $Cd(py)_2Hg(CN)_4$. We report here an infrared spectroscopic study of these complexes with the aim of searching for similar host structure to those found in the Hofmann–T_d–type clathrate compounds.

EXPERIMENTAL

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

$Cd(C_5H_5)N_2Cd(CN)_4$—. $Cd(CN)_2$ (4 m mol.) was dissolved in water. To this was added pyridine (4 m mol.). The white precipitate was filtered, washed with water, ethanol and ethere successively, and preserved in a desiccator.

$Cd(C_5H_5N)_2Hg(CN)_4$—. The preparation of this complex was similar to the previous one. A solution of $Cd(CN)_2$ (2 m mol.) and $Hg(CN)_2$ (2 m mol.) was used instead of 4 m moles of $Cd(CN)_4$.

The complexes were analyzed for C, H and N with the results as follows (%): Calculated for $Cd(C_2H_2N)_2$ $Cd(CN)_4$: C, 34.5; H, 2.1; N, 17.3. Found: C, 32.1; H, 2.1; N, 15.9; Calculated for $Cd(C_2H_2N)_2$ $Hg(CN)_4$: C, 29.2; H, 1.8; N, 14.6. Found: C, 28.2; H, 2.2; N, 14.2.

Spectra: Perkin-Elmer 1330 spectrometer was used to record the spectra of nujol and poly-chlortrifluorethylen mulls, which was calibrated using polystyrene films.

RESULTS AND DISCUSSION

The infarred spectral features of $Cd(py)_2Cd(CN)_4$ and $Cd(py)_2$ $Hg(CN)_4$ complexes are very similar. These similarities between the two complexes suggest that they are resemble each other in structure.

Owing to lack of structural data, the assignment was made by treating pyridine molecules (C_{2v}) and $M(CN)_4$ ions (T_d) as isolated units. The frequencies of the observed bands in the infrared spectra of the complexes studied and the assignments made are given in Table 1 and

Table 1. Infrared Spectra of Pyridine in the Liquid And in the Metal Complexes (cm^{-1}).*●

(C_{2v})	Assignment	Py(liquid)*	Py-Cd-Ni*	Py-Cd-Cd	Py-Cd-Hg
A_1	1 ν (CH)	3053	3064 w	—	—
	2 ν (CH)	3053	3056 w	—	—
	3 ν (CH)	3036	3035 w	3044 w	3044 w
	4 ν (ring)	1582	1603 vs	1597 vs	1598 vs
	5 ν (ring)	1482	1486 s	1484 s	486 s
	6 δ (CH)	1217	1217 s	1217 s	1218 s
	7 δ (CH)	1080	1083	1082	1082 w
	8 ν (ring)	1029	1037 s	1036 s	1036 s
	9 ν (ring)	990	1011 s	1011 s	1009 s
	10 δ (ring)	604	628 s	627 s	627 s
B_1	11 ν (CH)	3079	3082 m	3082	3084 w
	12 ν (CH)	3026	3021 w	3018 w	3018 w
	13 ν (ring)	1574	1575 m	1572 m	1572 m
	14 ν (ring)	1438	1446 vs	1443 s	1443 s
	15 ν (ring)	1355	1356 w	1358 v	—
	16 δ (CH)	1235	1236 w	1236 vw	1236 vw
	17 δ (CH)	1147	1152 s	1152 s	1151 s
	18 δ (CH)	1068	1065 s	1068 s	1068 s
	19 δ (ring)	650	650 w	651 vw	651 vw
A_2	20 γ (CH)				
	21 γ (CH)	infrared inactive, Raman active			
	22 γ (CH)		384		
B_2	23 γ (CH)	939	946 m	947 w	946 w
	24 γ (CH)	882	872	874 vw	874 vw
	25 γ (ring)	746	748 s	751 s	750 s
	26 γ (CH)	703	690 vs	691 vs	690 vs
	27 γ (ring)	405	413 m	411gw	411 w

Table 1. (Continued)

Assignment	py(linguid)*	Py-Cd-Ni*	Py-Cd-Cd	Py-Cd-Hg
Binary Combinations and Overtones*				
2 ν_{16}	or $\nu_4 + \nu_{24}$	—	2470	2470
2 ν_{17}		—	2304	2304
$\nu_1 - \nu_{18}$		—	1997	1997
$\nu_8 - \nu_{73}$		—	1979	1979
$\nu_7 + \nu_{24}$	or $\nu_9 + \nu_{23}$	—	1952	1952
$\nu_{12} - \nu_7$		—	1938	1938
$\nu_{10} + \nu_{10}$	or $\nu_{23} + \nu_{95}$	—	1693	1692
$\nu_{10} + \nu_8$		—	1663	1663
$\nu_9 + \nu_{10}$		1643	1538	1638
2 ν_{25}		—	1500	1500
$\nu_{19} + \nu_{25}$		—	1378	1378
2 ν_{19}		—	1303	1303
2 ν_{22}		—	770	770
$\nu_{22} - \nu_{26}$		—	304	304

● ν, δ and γ indicate valence, fn-plane, and out-of-plane vibrations, respectively; v= very, w= weak, m= medium, s= strong; py= pyridine, py-Cd-Ni= $Cd(Py)_2$ $Ni(CN)_4$, py-Cd-Cd= $Cd(Py)_2$ $Cd(CN)_4$, py-Cd-Hg= $Cd(Py)_2$ $Hg(CN)_4$

+ From Akyüz et al. 1973.

* 9nfrared active binary products: A^2_1,A^2_2,B^2_1,B^2_2, A_1xB_1, A_1xB_2, B_1xA_2 and A_2xB_2.

Table 2 for pyridine and $M(CN)_4$ ions, respectively, together with some pertinent spectral data [Akyüz, 1973] for comparison. The unassigned bands are given in Table 2.

Table 2. Infrared Spectra of $M(CN)_4$ (M= Ni, Cd or Hg) Group of the Metal Complexes (Cm$-_{2}^{1}$)●

(T_d) Assignment	$Cd(CN)_4$*	$Hg(CN)_4$*	$Cd(CN)_4$	$Hg(CN)_4$
A_1, ν_1 (CN)	2149	2149	(2180)	(2180)
A_1, ν_2 (M–C)	324	335	—	—
E, ν_3 (MCN)	—	—	—	—
E, ν_4 (GMC)	—	—	—	—
F_2, ν_5 (CN)	2145	2146	2173 vs	2173 vd
Hot band	—	—	2134 w	2140 w
$\nu(^{13}CN)$	—	—	2124 vw	2124 vw
F_2, ν_6 (Mixture of MC and MCN)	316	330	369 vs	369 vs
F_2, ν_7 (mixture of MC and MCN)	250	235	260 s	260 s
F_2, ν_8 (CMC)	(61)	(54)	—	—
F_1, ν_9 (MCN)	(194)	(180)	—	—
Combinations				
$\nu_1 - \nu_7$			1920 w	1920 w
$\nu_1 - \nu_6$			1813 w	— w
$\nu_5 - \nu_6$			1800 w	1802 w

Unassigned bands-For $Cd(Py)_2$ $Cd(CN)_4$: 1869, 1849, 1683, 1510, 1293, 1168, 969, 919, 890, 880, 857, 704, 679, 326, 302, 247; For $Cd(Py)_2$ Hg $(CN)_4$: 1869, 1984, 1510, 1293, 1167, 1108, 969, 918, 890, 877, 857, 703, 679, 600, 354, 326, 302 and 247.

● The bands assigned from combination bands are given in parentheses; v= very, w= weak, s= strong.

* From (Jones, 1961).

Vibrational spectra of pyridine and coordinated pyridine in metal complexes have been extensively studied by several workers. The most relevant work for our purpose is that of Akyüz et al. [Akyüz et al. 1973]. These authors presented infrared and Raman spectral data for a series of Hofmann type pyridine complexes with the formula $M(py)_2$ $Ni(CN)_4$ (M= Mn, Co, Fe, Ni, Cu, Zn and Cd). They made the assignment of vibrations of coordinated pyridine by making a one to one comparison with the assignments for liquid pyridine (Table 1). The upward shifts of several fundamental frequencies of pyridine in complexes when compared to those of free molecule were mainly explained in terms of coupling of the internal vibrational modes of the pyridine with the M–N vibrations. Their explanation was supported for in plane modes by a simple normal coordinate analysis.

A glance at Table 1 shows that each of the fundamental frequencies in the spectrum of $Cd(py)_2Ni(CN)_4$ is faitfully reproduced with only minor shifts in the spectra of $Cd(py)_2Cd(CN)_4$ and $Cd(py_2)_2Hg(CN)_4$ complexes. The striking correspondance between these frequencies is strong support for the conclusion that pyridine molecules in our complexes coordinate to Cd.

Infrared active fundamental bands attributable to coordinated pyridine (C_{2v}) in the complexes were assigned by making one to one comparison with the infarred band assignments for $Cd(py)_2Ni(CN)_4$ complex and neat pyridine as given in Table 1. In addition to these, we observed a number of weak bands; those of which assigned to binary combination and overtone vibrations are listed in Table 1.

In assigning the observed infrared bands attributable to $M(CN)_4$ (M= Cd or Hg) ions in our complexes, we refer to the work of Jones [Jones, 1961]. Jones presented vibrational data for the salts $K_2Cd(CN)_4$ and $K_2Hg(CN)_4$ the solid state and assigned the ınfrared and Raman active fundamental vibrations of the isolated $Cd(CN)_4$ and $Hg(CN)_4$ ions on the basis of T_d symmetry. These are given in Table 2. for comparison with the assignments for $M(CN)_4$ groups in our complexes.

In the infrared spectra of $Cd(py)_2M(CN)_4$ (M=Cd or Hg) complexes, three strong bands at 2173, 360 and 260 cm^{-1} arise from $M(CN)_4$ ions. The band at 2173 cm^{-1} is assigned to υ_5 (asymmetric CN str., F_2). This assignment is in agreement with that of 2171 cm^{-1} band observed in the infrared and Raman spectra of the T_d-type $Cd(NH_2)_3M(CN)_4$ (M= Cd or Hg) clathrates [Iwamoto and Shriver, 1972)]. The bands at 369 and 260 cm^{-1} are assigned to υ_6 and υ_7 (both are mixture of MC str. and NCM bend., F_2), respectively. The measured frequencies (2173, 369 and 260 cm^{-1}) appear to be much higher than those measured for isolated $Cd(CN)_4$ or $Hg(CN)_4$ ions (Table 2). Such frequency shifts have been observed for many other compounds, including Hofmann type compounds, in which the both ends of CN group are coordinated [see for example. Akyüz et al., 1973; Kantarcı, 1983; Ağustoslu et al., 1984; Sungur and Akyüz, 1987]. For the $Ni(CN)_4$ group in the Hofmann type complexes, the upward shifts compared to those of isolated $Ni(CN)_4$ ion were mainly explained as the mechanical coupling of the internal modes of $Ni(CN)_4$ with the M–N and also with other low frequency vibrations [Akyüz, 1973]. Then, the spectral data indicate that the N-ends of $M(CN)_4$ group in our complexes bound to Cd.

Three weak bands at 1800, 1813 and 1920 cm^{-1} in the infarred spectra of complexes may be assigned to $\upsilon_5 - \upsilon_6$, $\upsilon_1 - \upsilon_6$ and $\upsilon_1 - \upsilon_7$, respectively. From the combinations $\upsilon_1 - \upsilon_6$ and $\upsilon_1 - \upsilon_7$, a wavenumber of 2180 cm^{-1} is deduced for the Raman active mode υ_1 (symmetric CN str., A_1).

The preceeding discussions, considered together, lead us to draw the conclusion that the frameworks of the complexes $Cd(py)_2M(CN)_4$ (M= Cd or Hg) are similar to those found in Hofmann-Td-type clatharte compounds.

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