

FT-IR Spectroscopic Investigation of Hofmann Td-Type Complexes of 2-, and 3-Chloropyridine

SEVIM AKYUZ^{1*}, MERIC BAKILER², LILJANA ANDREEVA³ and BILJANA MINCEVA-SUKAROVA³

¹Istanbul University, Department of Physics, Vezneciler, 34459, Istanbul, Turkey; ²Mimar Sinan University, Department of Physics, Besiktas, 80690, Istanbul, Turkey; ³Institute of Chemistry, Faculty of Science, Sts. Cyril & Methodius University, Arhimedova 5, POB 162, MK-1000 Skopje, Macedonia

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Abstract

Hofmann-type modified clathrate hosts containing 2- or 3-chloropyridine molecules attached to metal (II) tetracyanocadmate frame, with a given formula: $M(\text{Clpy})_2\text{Cd}(\text{CN})_4$, where $M = \text{Mn}, \text{Ni}$ or Cd ; Clpy = 2- or 3-chloropyridine, have been synthesised for the first time. Their FT-IR spectra are reported in the $400\text{--}4000\text{ cm}^{-1}$ region. All the vibrational modes of coordinated Clpy are characterised. The spectral features of the compounds studied are found to be similar to each other indicating that they have analogous structures. The coordination effect on the Clpy modes is analyzed.

Introduction

The well-known Hofmann Td-type clathrate host with the given formula $M(\text{NH}_3)_2\text{Cd}(\text{CN})_4$ is comprised of a 3-dimensional network constructed by the alternate linkage between tetrahedral Cd(II) and octahedral M(II) through the cyanide bridges. The Cd(II) atom in $\text{Cd}(\text{CN})_4$ moieties is tetrahedrally coordinated to the C atoms of four cyanide groups. The octahedral coordination of M(II) atom is accomplished by six nitrogen atoms; two are from the two ammonia ligands attached to the M atom in trans position to each other, other four are from cyanide groups [1]. Several Td-type host structures have been developed from that of Hofmann Td-type clathrate hosts by replacing two ammonia ligands by other N- or O-donor ligands [2]. In this study we report the IR spectra of six new Hofmann Td-type host structures, $M(\text{Clpy})_2\text{Cd}(\text{CN})_4$ $\{M = \text{Mn}, \text{Ni}, \text{or Cd}; \text{Clpy} = 2\text{- or }3\text{-chloropyridine, abbreviated hence for as } M\text{-Cd-Clpy}\}$. The aim of this study is to give further examples of Hofmann-type host structures and to investigate 2-Clpy and 3-Clpy vibrations in isostructural complexes.

Experimental

All chemicals used were reagent grade (Merck) and used without further purification. The compounds were prepared by adding 1 mmol solution of $\text{K}_2\text{Cd}(\text{CN})_4$ and slightly higher than 2 mmol Clpy to 1 mmol MCl_2 solution in constant stirring. The precipitate formed was filtered, washed

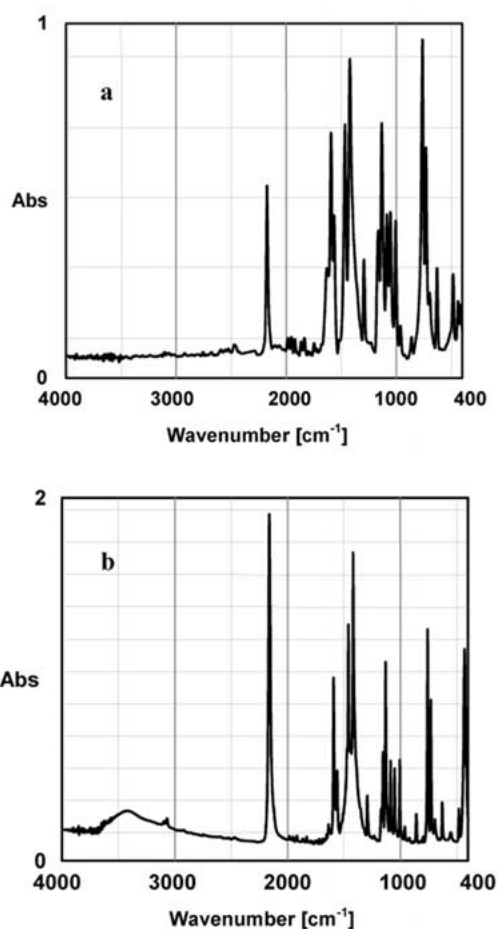


Figure 1. FT-IR spectra of $\text{Cd}(\text{2Clpy})_2\text{Cd}(\text{CN})_4$ (a), and $\text{Ni}(\text{2Clpy})_2\text{Cd}(\text{CN})_4$ (b).

* Author for correspondence. E-mail: sakyuz@istanbul.edu.tr

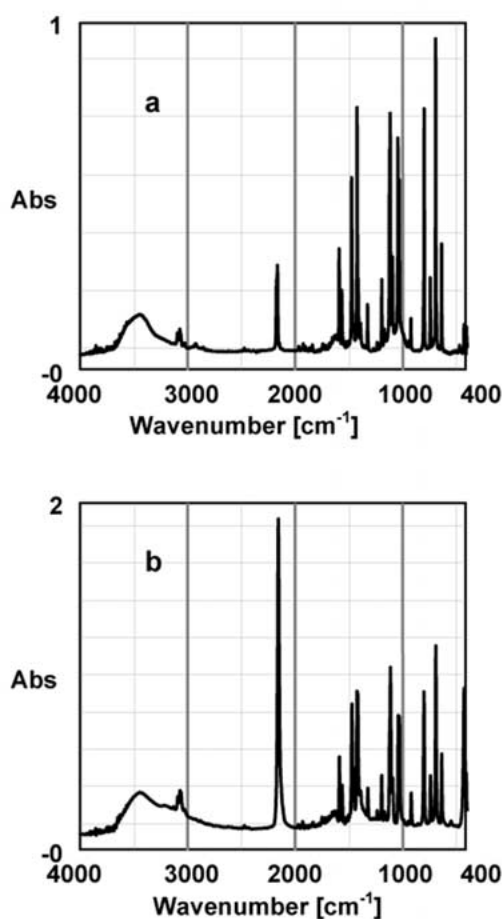


Figure 2. Ni(3Clpy)₂Cd(CN)₄ (b).

with water, ethanol and ether successively and kept in a desiccator. The freshly prepared compounds were analysed for metal content by using the XRF technique.

The IR spectra (4000–400 cm⁻¹) of nujol mulls or KBr discs were recorded on a Jasco 300E FT-IR spectrometer (2 cm⁻¹ resolution).

Results and discussion

The FT-IR spectra of Cd-Cd-2Clpy and Ni-Cd-2Clpy complexes are given in Figure 1a and b respectively. The FT-IR spectra of Cd-Cd-3Clpy and Ni-Cd-3Clpy complexes are given in Figure 2a and b, respectively. The IR spectral features of the M-Cd-2Clpy or M-Cd-3Clpy complexes are found to be similar to each other indicating that they have analogous structures. The vibrational wavenumbers of 2- and 3-Clpy in M-Cd-Clpy complexes are tabulated in Tables 1 and 2 together with the relevant data [3].

The vibrational wavenumbers of 2- or 3-Clpy show all the characteristics of coordinated pyridine derivatives. Several modes of Clpy, particularly the ring breathing mode in M-Cd-Clpy compounds show upward frequency shifts compared to those of free molecules. In our previous papers [4, 5] the IR spectrum of coordinated 2- and 3-Clpy were calculated and it was concluded that the alteration of the

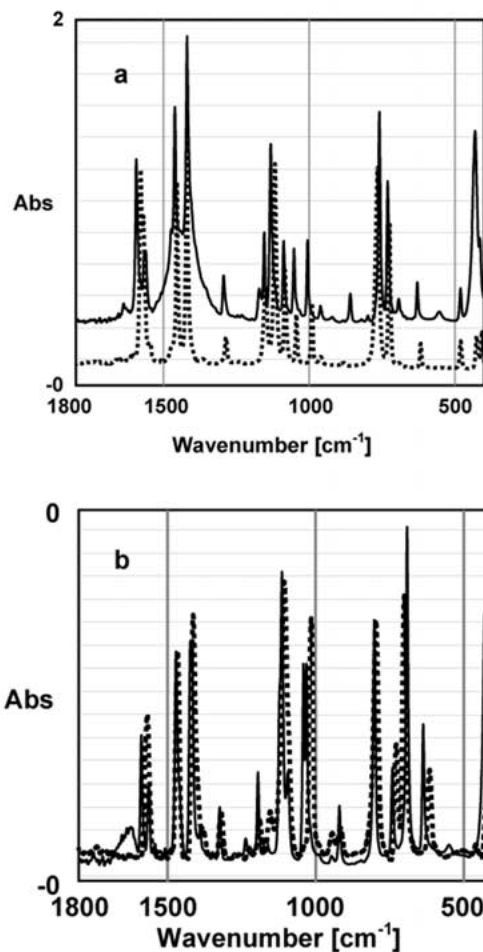


Figure 3. 400–1800 cm⁻¹ region of the IR spectra of liquid 2Clpy (dotted line) together with Ni(2Clpy)₂Cd(CN)₄ complex (solid line) (a), liquid 3Clpy (dotted line) together with Ni(3Clpy)₂Cd(CN)₄ complex (solid line) (b).

electron distribution and the force field of the coordinated 2- or 3-Clpy with respect to the free molecule was mainly responsible for these frequency shifts. Moreover the kinematic interaction of the vibrational modes of the ligand molecule by metal ligand bond vibrations has an additional contribution to the frequency shifts. The FT-IR spectra of the 400–1800 cm⁻¹ region of the Ni-Cd-2Clpy and Ni-Cd-3Clpy complexes studied are shown in Figure 3, together with that of liquid 2Clpy or 3Clpy, respectively. As seen in Figure 3a and b and Tables 1–2, the vibrational modes of Clpy in M-Cd-Clpy compounds show the characteristic blue shifts for the coordinated ligand, with respect to the free molecule.

The 2- and 3-Clpy wavenumbers of M-Cd-Clpy are compared to the corresponding ones of the IR spectral data of Hofmann-type complexes of 2- and 3-Clpy M(Clpy)₂Ni(CN)₄; Clpy = 2- or 3-Clpy and M = Mn, Ni or Cd [6, 7]. The wavenumber shifts observed upon coordination of 2- or 3-chloropyridine to the metal (II) are found to be similar in both complexes, indicating that the crystal structure does not contribute much to the coordination effects of the ligand. The ring breathing modes of these complexes are given in Table 3.

Table 1. Vibrational wavenumbers of 2-chloropyridine in M-Cd-2Clpy complexes

Assignment ^d	2Clpy		M-Cd-2Clpy		
	IR ^a	IR	Cd	Mn	Ni
<i>A'</i>					
$\nu(\text{CH})$	3082 sh	3084 sh	3086	3090 vw	3099 w
$\nu(\text{CH})$	3082 sh	3075 sh	–	–	3078 sh
$\nu(\text{CH})$	3059 s	3055 vs	3066 vw	3069 vw	3073 m
$\nu(\text{CH})$	3059 s	3003 m	3054 vw	3054 vw	3055 w
ν_{ring}	1577 s	1577 vs	1592 vs	1590 vs	1593 vs
ν_{ring}	1568 s	1568 s	1567 s	1569 s	1567 s
ν_{ring}	1452 s	1453 vs	1473 w	1473 w	1473 w
			1564 s	1463 s	1461 s
ν_{ring}	1420 s	1420 s	1422 s	1422	1419 vs
ν_{ring}	1363 w	1365 w	1389 vw	1388 vw	1387 vw
$\delta(\text{CH})$	1286 m	1286 s	1295 s	1293 m	1294 m
$\delta(\text{CH})$	1148 s	1149 vs	1157 s	1156 s	1154 s
X-sens.	1117 vs	1117 vs	1132 vs	1130 vs	1132 vs
$\delta(\text{CH})$	1083 s	1083 vs	1088 vs	1087 s	1088 s
$\delta(\text{CH})$	1044 s	1045 s	1052 vs	1049 s	1052 s
Ring breath.	992 s	991 s	1005 vs	1003 s	1006 s
X-sens.	725 s	724 vs	732 s	730 vs	731 vs
δ_{ring}	617 m	617 m	630 s	626 s	630 s
X-sens.	425 m	426 m	438 s	437 vs	431 vs
<i>A''</i>					
γCH	960 w	961 w	962 m	963 m	962 m
γCH	–	914 w	919 w	918 w	921 w
γCH	881 w	878 w	891 w	890 w	888 w
γCH	767 s	767 vs	761 vs	765 vs	759 vs
γ_{ring}	–	691 w	695 m	694 m	693 m
γ_{ring}	480 m	480 s	482 s	483 s	481 s
γ_{ring}	406 w	407 m	415 s	412 s	415 s

^aAssignment and wavenumbers are taken from ref. Green *et al.* [3].

The cyanide stretching wavenumbers of the $\text{Cd}(\text{CN})_4$ group are tabulated in Table 4 together with the IR data of $\text{K}_2\text{Cd}(\text{CN})_4$ salt [8] and Hofmann Td-type pyridine complexes, $\text{M}(\text{py})_2\text{Cd}(\text{CN})_4$, [9]. In $\text{K}_2\text{Cd}(\text{CN})_4$ salt, the $\text{Cd}(\text{CN})_4$ ion can be treated as an isolated unit with Td symmetry. Therefore, when CN-M coordination takes place (e.g. in M-Cd-Clpy) upward wavenumber shifts in CN modes are expected, due to the coupling with M-N (NC) bond vibrations [10]. This is what we observed: in the IR spectra of the M-Cd-Clpy compounds (see Table 4). The CN stretching vibrational mode (F_2) is observed as one strong band in M-Cd-Clpy complexes except for Cd-Cd-3Clpy. In the case of Cd-Cd-3Clpy this band was observed as a split pair at Cd-Cd-3Clpy complex, indicating the presence of a slight distortion in the later complex. On the other hand cyanide stretching vibrational wavenumbers of the $\text{Cd}(\text{CN})_4$ group of the complexes studied, are found to be higher than that of $\text{K}_2\text{Cd}(\text{CN})_4$ but close to those of $\text{M}(\text{py})_2\text{Cd}(\text{CN})_4$, indicating that CN-M coordination takes place, and the structure is the same as Hofmann Td-type clathrate hosts. In the Hofmann Td-type host lattices, two type of cavities, α and β are formed in the 3-dimensional lattice. The cavity α , in the flexible 3-dimensional lattice of the Hofmann Td-type pyridine host, $\text{M}(\text{py})_2\text{Cd}(\text{CN})_4$, is occupied by the pyridine ligand but

cavity β collapses with no room for any guest [11]. It must be noted that all our efforts for trapping benzene molecules into the cavities of the M-Cd-Clpy compounds failed.

In conclusion, based on the spectroscopic results, we propose that M-Cd-Clpy compounds are substantially isostructural to those of the already known Hofmann Td-type pyridine host lattice [11].

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Table 2. Vibrational wavenumbers of 3-chloropyridine in M-Cd-3Clpy complexes

Assignment ^a	3Clpy		M-Cd-3Clpy		
	IR ^a	IR	Cd	Mn	Ni
A'					
$\nu(\text{CH})$	–	3128 vw	3094 m	3095 m	3090 m
$\nu(\text{CH})$	–	3073 sh	3072 m	3072 m	3072 m
$\nu(\text{CH})$	3052 s	3044 s	3065 m	3066 m	3061 m
$\nu(\text{CH})$	3052 s	3019 m	3032 w	3034 w	3031 w
ν_{ring}	1573 s	1571 vs	1590 vs	1591 vs	1588 vs
ν_{ring}	1569 s	1562 sh	1566 s	1566 s	1563 s
			1560 s	1560	
ν_{ring}	1469 vs	1467 s	1473 vs	1473 vs	1471 vs
ν_{ring}	1417 vs	1415 s	1423 vs	1421 vs	1423 vs
					1418 vs
ν_{ring}	1319 m	1319 m	1326	1389 vw	1324 m
$\delta(\text{CH})$	1227 w	1225 vw	1236 w	1235 w	1236 w
$\delta(\text{CH})$	1190 m	1189 m	1193 s	1194 s	1195 s
$\delta(\text{CH})$	1106 vs	1106 vs	1117 vs	1118 vs	1114vs
X-sens.	1095 vs	1094 s	1093 m	1095 m	1093 m
$\delta(\text{CH})$	103 4m	1036 vw	1044 vs	1043 vs	1040 s
Ring Breath.	1016 vs	1015 vs	1032 vs	1033 s	1031 s
X-sens.	728 vs	729 s	743	742 s	741 s
δ_{ring}	615 s	615 m	637 m	637 s	637 s
X-sens.	426 s	425 m	428 m		
A''					
γCH	[980]	989 sh	991 vw	993 vw	988 w
γCH	943 m	944 w	943 vw	942	947 vw
γCH	915 m	916 w	923 w	923	920 m
γCH	796 vs	795 vs	800 s	799 vs	802 vs
γ_{ring}	700 vs	701 vs	692 vs	693 vs	691 vs
γ_{ring}	461 w	459 vw	458 w		
			471 m		
γ_{ring}	403 m	401m	406 m		409 s

^aAssignment and wavenumbers are taken from ref. Green et al. [3].

Table 3. The vibrational wavenumbers (cm^{-1}) of the ring breathing mode of 2-and 3-chloropyridine in Hofmann Td-type and Hofmann-type complexes

2Clpy	Hofmann Td-type M-Cd-2Clpy ^a				Hofmann-type M-Ni-2Clpy ^b		
	Liquid	Mn	Ni	Cd	Mn	Ni	Cd
Ring breathing	991 s	1003 s	1006 s	1005 vs	1004 vs	1008 vs	1006 vs
3Clpy							
	Hofmann Td-type M-Cd-3Clpy ^a				Hofmann-type M-Ni-3Clpy ^c		
Ring breathing	1015 vs	1033 vs	1031 s	1032 vs	1031 vs	1034 vs	1030 vs

^aThis study.

^bTaken from Akyuz *et al.* [7].

^cTaken from Akyuz *et al.* [6].

Table 4. Cyanide stretching vibrational wavenumbers of $\text{Cd}(\text{CN})_4$ group

Assignment ^a	$\text{K}_2\text{Cd}(\text{CN})_4$ [^b]	Pyridine ^a		M-Cd-2Clpy			M-Cd-3Clpy		
		Cd	Mn	Mn	Ni	Cd	Mn	Ni	Cd
$\nu_5(\text{CN}) \text{F}_2$	2145	2173	2170	2168 s	2163 vs	2174 s	2165 s	2156 vs	2172 2165

^a $\text{M}(\text{pyridine})_2\text{Cd}(\text{CN})_4$ taken from ref. Kantarci *et al.* [9].

^b $\text{K}_2\text{Cd}(\text{CN})_4$ taken from ref. Jones [8].

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