

Vibrational Spectroscopic Study of 1*H*-1,2,4-Triazole Hofmann-T_d-Type Complexes

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Hofmann-T_d-type modified hosts containing 1*H*-1,2,4-triazole molecule attached to M(II) tetracyanocadmate frame, with a given formula: M(Htrz)₂M'(CN)₄, where M = Mn; M' = Zn, Cd or Hg; M = Cd, M' = Cd or Hg; Htrz = 1*H*-1,2,4-triazole, have been synthesized. Their elemental analyses, FT-IR (4000-400 cm⁻¹) and the FT-Raman spectra (4000-50 cm⁻¹) are reported for the two [Cd(Htrz)₂Cd(CN)₄] and [Cd(Htrz)₂Hg(CN)₄] of these complexes. All the vibrational modes of coordinated Htrz are characterised. The spectral features of the compounds studied are found to be similar to each other indicating that they have analogous structures.

Key Words: 1*H*-1,2,4-Triazole, Hofmann-T_d-type complexes, FT-IR and FT-Raman spectra.

INTRODUCTION

The 1,2,4-triazole compounds are considered interesting heterocycles since they possess important pharmacological activities such as antifungal and antiviral activities^{1,2}. Many 1,2,4-triazoles having different functionalities are used as dyes and photographic chemicals. Polymers derived from triazoles currently embody the most important practical application of this heterocyclic system^{1,2}. Metal coordination compounds with 1,2,4-triazoles and its derivatives have recently been reviewed by Haasnoot³. The vibrational modes of 1,2,4-triazole have been given by Billes *et al.*⁴ and Billing⁵. The compounds possessing this type of host framework reported to date have been confined to the Mn or Cd metal atom in an octahedral environment and to the Cd or Hg metal atom in a tetrahedral group⁶⁻¹². Hofmann-T_d-type host structures are defined with the general formula of M(L)₂M'(CN)₄ where M is one of the first row transition metals, L₂ corresponds to a pair of monodentate ligand molecules and M' is for Zn, Cd or Hg. The host structure is formed by the chains of -M-L₂-M'-L₂ extending along the a- and b- axes alternately and the tetrahedral M'(CN)₄ ions are arranged between the consecutive crossing chains with the N-ends bound to the M atoms⁶⁻⁸. This structure possesses two kinds of cavities, namely α and β. The α cavity with the rectangular box is similar to those in the Hofmann type hosts while the β cavity is a twisted biprism^{7,8}. The cavities within the structure can act as a host for the guest molecules.

In previous studies a number of clathrate compounds possessing this type of host structure have been reported⁶⁻¹². Now,

we have prepared five new complexes of the form M(L)₂M'(CN)₄ (M = Mn; M' = Zn, Cd or Hg; M = Cd, M' = Cd or Hg; L = 1*H*-1,2,4-triazole) (abbr. M-M'-L; Htrz = 1*H*-1,2,4-triazole). In this study, the infrared spectra of these compounds and Raman spectra of Cd-Cd-Htrz and Cd-Hg-Htrz (Raman spectra could not be obtained for the beige Mn-M'-Htrz compounds) reported. The aim of the study is to give further examples of Hofmann-T_d-type host structures and to investigate Htrz vibrations in isostructural complexes. These complexes are analogous to the Hofmann-T_d-type complexes and clathrates⁶⁻⁸.

EXPERIMENTAL

All chemicals used were reagent grade (Merck) and used without further purification. The complexes Mn-M-Htrz (M = Zn, Cd or Hg) were synthesized by adding 1 mmol of Htrz and 1 mmol of K₂M(CN)₄ solution in water to 1 mmol of MnCl₂ solution in water. The beige powder precipitate was filtered, washed with water, ethanol and ether, successively and kept in a desiccator containing molecular sieve. The Cd-Cd-Htrz and Cd-Hg-Htrz complexes were prepared using a method analogous to that given in the literatures⁹⁻¹².

The freshly prepared compounds were analyzed for C, H and N by a Carlo Erba 1108 elemental analyzer with the results as follows (found %/calcd. %). Cd(C₂H₃N₃)Cd(CN)₄: C = 20.52/20.57, H = 1.23/1.29, N = 29.94/29.99; Cd(C₂H₃N₃)Hg(CN)₄: C = 17.37/17.40, H = 1.04/1.09, N = 25.31/25.36; Mn(C₂H₃N₃)Zn(CN)₄: C = 26.45/26.50, H = 1.62/1.66, N = 38.60/38.63; Mn(C₂H₃N₃)Cd(CN)₄: C = 23.41/23.46, H = 1.45/1.47, N = 34.14/34.20; Mn(C₂H₃N₃)Hg(CN)₄: C = 19.24/19.30, H = 1.18/1.21, N = 28.11/28.14.

Physical measurements: The FT-IR spectra of discs (KBr) and mulls (nujol) of fresh samples, were recorded on Perkin Elmer 1330 and Mattson 1000 FT-IR spectrometers, which were calibrated using indene and polystyrene film. FT-Raman spectra were recorded using a Bruker RFS 100/S FT-Raman spectrometer in the range 4000-50 cm^{-1} . The 1064 nm line, provided by a Nd: YAG air-cooled laser, was used as excitation line. A liquid nitrogen cooled Ge detector was used. The output laser power was set to 40-60 mW.

RESULTS AND DISCUSSION

The complexes under study show no much differences between the infrared spectra recorded in Nujol (or fluoroube) mulls and KBr pellets. The FT-IR and Raman spectra of Htrz and Cd-Htrz-Cd complex are shown in Figs. 1(a-b) and Figs. 2(a-b), respectively. The vibrational spectral features of the compounds $M(\text{Htrz})_2M'(\text{CN})_4$ ($M = \text{Mn}$; $M' = \text{Zn}$, Cd or Hg; $M = \text{Cd}$, $M' = \text{Cd}$ or Hg) are found to be very similar, suggesting that they have isomorphous crystal structures.

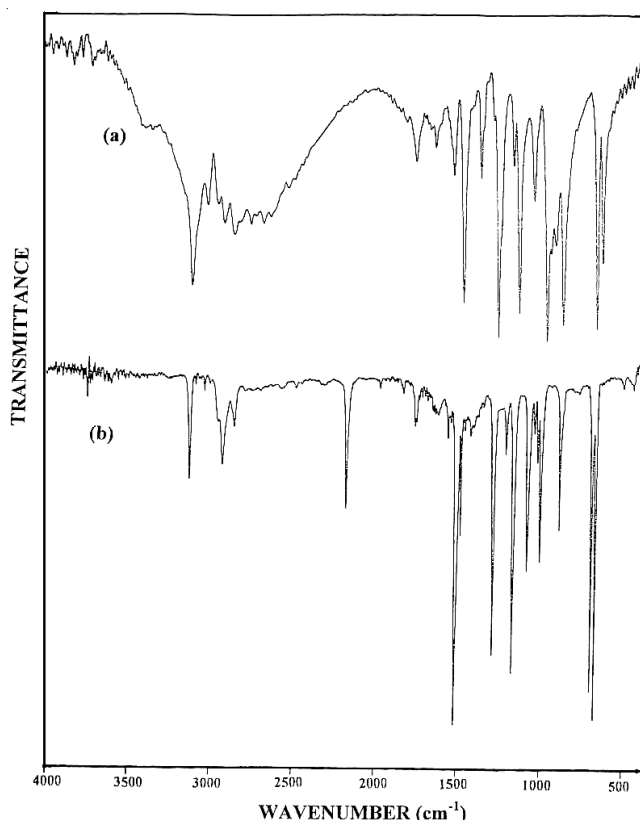


Fig. 1. FT-IR spectra of the 1H-1,2,4-triazole (a) and the Cd-Htrz-Cd complex (b)

Because of the lack of structural data for the compounds studied, the vibrational assignment was made by treating the 1H-1,2,4-triazole and the $M'(\text{CN})_4$ ($M' = \text{Zn}$, Cd or Hg) ions as isolated units. The FT-IR and FT-Raman wavenumber and the assignments made are given for Htrz and $M'(\text{CN})_4$ units in Tables 1 and 2, respectively along with some relevant spectral data for comparison.

1H-1,2,4-Triazole (Htrz) vibrations: The fundamental vibrational modes of 1H-1,2,4-triazole ($\text{C}_3\text{H}_3\text{N}_3$) have been assigned by many authors^{4,5,13,14}. This molecule belongs to

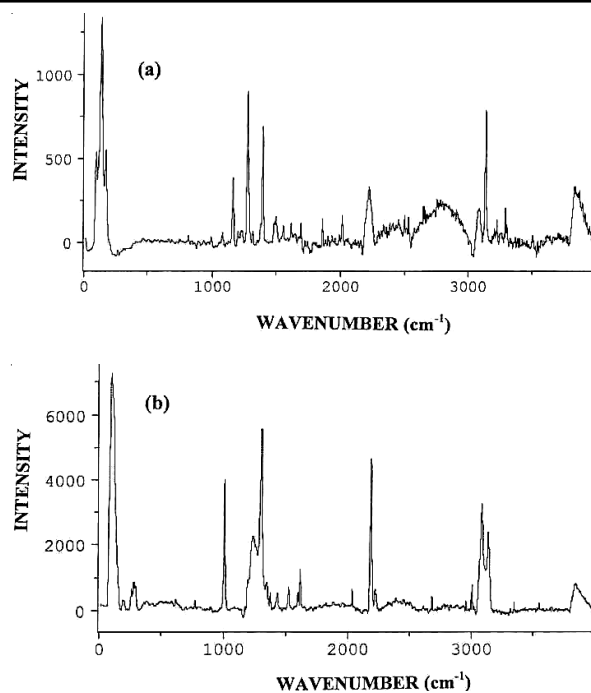


Fig. 2. FT-Raman spectra of the 1,2,4-triazole (a) and the Cd-Htrz-Cd complex (b)

C_s point group and there will be 18 modes of vibrations which are divided among the symmetry species as follows: 13A' and 5A'' (all IR and Raman active). The vibrational wave numbers of 1H-1,2,4-triazole observed in the infrared spectra of the complexes are given in Table-1. A comparison of the FT-IR and FT-Raman spectra of the ligand and complexes highlights the following facts.

The interpretation of the vibrational spectra of the 1H-1,2,4-triazole is difficult since the spectra reflects strong associations in condensed state. Therefore, the region above 2000 cm^{-1} is full of overlapping broad bands in the infrared and Raman spectra (Figs. 1a and 2a) and the experimental assignment of the bands here is not straightforward. Band decomposition can help in the interpretation. Since one of the resolved bands was chosen for the NH stretching band, this assignments is uncertain to a certain extent. Raman spectra are decisive here although the intensities of the $\nu(\text{NH})$ bands are very low.

For 1H-1,2,4-triazole several tautomeric forms (Fig. 3) can be envisaged in the isolated state. The wave numbers of the fundamental vibrations of Htrz in powder form and their assignment given by Billes *et al.*⁴, is presented in Table-1. Table-1 also tabulates the wave numbers predicted from the PED (potential energy distribution)⁴. The infrared data on some Htrz metal complexes were reported by Billing⁵, who gave approximate interpretations of the vibrational modes of the molecule and its metal(II) halide Htrz complexes.

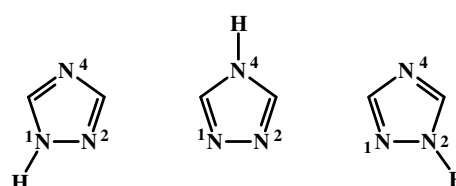


Fig. 3. Tautomers of 1,2,4-triazole

TABLE-1
VIBRATIONAL WAVENUMBERS (cm⁻¹) OF 1*H*-1,2,4-TRIAZOLE IN THE COMPLEXES

1 <i>H</i> -1,2,4-Triazole			V _{cal} ^a	CuCl ₂ Htrz ^c	Cd-Htrz-Cd	Cd-Htrz-Hg	Mn-Htrz-Zn	Mn-Htrz-Cd	Mn-Htrz-Hg	Assignment ^a		
(IR)v _{exp}		Raman		IR	IR Raman	IR Raman	IR	IR	IR			
[a]	[b]	[b]		IR	IR Raman	IR Raman	IR	IR	IR	PED (%)		
A'	3446	3416 vw 3287 w	3446	–	no	no	no	no	no	no	vNH (99)	
	3119	3128 m 3132 s	3108	–	3124 m	3133 m	3122 m	3130 m	3117 m	3119 m	3118 m	vCH (99)
	3098	3093 w 3077 w	3101	–	3091 w	3077 m	3091 w	3077 m	3089 w	3089 m	3085 m	vCH (99)
	1482	1483 vs 1490 w	1489	1500 mw, b	1508 vs	1513 w	1509 vs	1515 w	1501 vs	1506 vs	1509 vs	vrg(53) + βCH(40)
	–	–	–	1481 mw, b	1478 m	–	1477 m	–	1475 m	1473 m	1476 m	–
	1379	1379 m 1381 s	1385	1423 ms	1456 vw	1421 w	1453 vw	1423 w	1454 vw	1455 vw	1453 w	vrg(43) + βCH(24) + βNH(25)
	–	–	–	1415 ms	–	–	–	–	–	–	–	–
	1361	–	1336	–	–	–	–	–	–	–	–	vrg(43) + βCH(27) + βNH(20)
	1272	1273 vs 1263 s	1265	1312 ms	1279 vs	1335 w	1278 vs	1331 w	1280 vs	1278 vs	1277 vs	vrg(69) + βCH(20)
	1255	1257 v,sh 1217 vw	1230	1236 mw	nm	1294 vs	nm	1293 vs	1234 vw	nm	nm	vrg(51) + βCH(39)
	1146	1181 w 1185 vw	1138	1210 mw	1206 w	1221 m	1205 w	1220 m	1205 w	1206 w	1203 w	vrg(70) + βCH(13) + βrg(15)
	1062	1147 vs 1149 m	1074	1165 m, b	1158 vs	1178 w	1158 vs	1175 w	1160 vs	1157 vs	1158 vs	vrg(62) + βNH(29)
	1054	1057 m 1066 vw	1045	1076 ms	1076 s	nm	1077 s	nm	1075 s	1078 s	1077 s	vrg(68) + βCH(19) + βrg(12)
	980	980 vs	977	–	997 s	993 s	995 s	992 s	995 s	992 s	991 s	vrg(23) + βrg(70)
	955	955 m	946	968 m, b	976 vw	–	976 vw	–	978 vw	976 vw	977 vw	vrg(13) + βrg(76)
A''	926	930 m	932	942 m, b	936 vw	–	939 vw	–	940 vw	936 vw	939 vw	γCH(94)
	884	883 vs	878	871 m	882 s	–	881 s	–	880 s	885 s	881 s	γCH(96)
	681	680 vs	674	730 ms, b	688 vs	–	686 vs	–	686 vs	687 vs	688 vs	γrg(94)
	649	647	656	622 ms	664 vs	–	661 vs	–	662 vs	663 vs	660 vs	γrg(88) + γNH(11)
	–	–	550	552 mw	–	–	–	–	–	–	–	γrg(16) + γNH(83)

^aTaken from Ref.-4. ^bThis work. ^cTaken from Ref.-5. (PED: potential energy distribution).

TABLE-2
VIBRATIONAL WAVENUMBERS (cm⁻¹) OF CYANIDE GROUP FOR THE M-M'-Htrz COMPLEXES

Assignment ^a	K ₂ Zn(CN) ₄ ^a	K ₂ Cd(CN) ₄ ^a	K ₂ Hg(CN) ₄ ^a	Cd-Htrz-Cd	Cd-Htrz-Hg	Mn-Htrz-Zn	Mn-Htrz-Cd	Mn-Htrz-Hg
v ₁ (CN) A ₁	(2157)	(2149)	(2149)	(2170 vs)	(2170 vs)	no	no	no
v ₅ (CN) F ₁	2152	2145	2146	2165 vs	2163 vs	2165 vs	2163 vs	2163 vs
v ₆ [v(MC)+δ(NCM)]F ₂	356	316	330	350 s	350 s	360 s	352 s	352 s
v ₇ [v(MC)+δ(NCM)]F ₂	315	250	235	261 w	261 w	270 w	267 w	267 w

The band observed in the Raman spectra are in given parentheses. ^aTaken from Ref.-16.

The ν(NH) stretching and N-H out-of-plane bending vibrations in the complexes are not observed. On the other hand, the ring breathing and C-H in-plane bending mode occurs at

1483 cm⁻¹ (FT-IR) and at 1490 cm⁻¹ (FT-Raman) in free Htrz ligand, while it is observed around 1508 cm⁻¹ (FT-IR) and 1513 cm⁻¹ (FT-Raman) in the metal complexes. Besides, several

modes of Htrz, particularly the ring stretching (1147 cm^{-1} FT-IR) and the ring in-plane breathing mode (1057 cm^{-1} FT-IR) in M-M'-Htrz complexes show upward frequency (1158 and 1076 cm^{-1} FT-IR, respectively) shift compared to those of Htrz molecules. We observed these modes in the Raman spectra at 1149 and 1066 cm^{-1} in free Htrz molecules. However, the ring stretching at 1149 cm^{-1} is observed at 1178 cm^{-1} in FT-Raman the above mentioned complexes, in the ring in-plane breathing mode complexes at 1066 cm^{-1} was not observed in the FT-Raman spectra (Table-1).

It is clear from Table-1 that most of the vibrational modes of Htrz in the complexes have increased in wave numbers when compared with free Htrz. These shifts may be explained as the coupling of M-N(Htrz) vibrations. Similar shifts have been observed in metal coordinated 1H-1,2,4-triazole complexes^{13,14}. Similar observations have been previously for pyridine nitrogen complex^{10,11,15}.

M'(CN)₄ group vibrations: In assigning the bands attributable to M'(CN)₄ (M' = Zn, Cd or Hg) ions in the spectra of present compounds, we refer to the work of Jones¹⁶ who presented vibrational data for the salts K₂M(CN)₄ (M = Zn, Cd or Hg) in the solid phase and assigned the infrared and Raman active fundamental vibrations of the M(CN)₄ ion on the basis of T_d symmetry. The assigned wave numbers for the M'(CN)₄ groups in the compounds studied appear to be much higher than those for M(CN)₄ groups in K₂M(CN)₄ (M = Zn, Cd or Hg) (Table-2). Such frequency shifts have been observed for other T_d-type clathrates^{7,8} and T_d-type host complexes¹⁹⁻¹²,

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 = Zn, Cd or Hg) with the M-NC vibrations. It follows that the N-ends of the M(CN)₄ groups are also bound to a M atom in present clathrate compounds.

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