

Synthesis, Crystal Structure and Characterization of [(CH₃ CH₂)₄N] Mn_{1.5} Cl₃ 4H₂O Cl 2(H₂O)

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Abstract

Single crystals of $[(CH_3CH_2)_4N]$ Mn_{1,5} Cl₃ 4H₂O Cl 2(H₂O) were grown by the slow evaporation technique and characterized by means of single-crystal X-ray diffraction, FT-IR and Raman spectroscopy. The title compound belongs to

the triclinic space group *P*1 with the following unit cell dimensions: a =7.5425(4) Å, b=9.8464 Å, c=13.7671(6) Å, α =89.951(3)°, β =89.753(3)°, γ =81.861(3)°, Z=4. These structures have solved using direct methods and refined by least-squares analysis. The structure was solved by the direct method and refined to final *R* value of 0.0567. The projection of [(CH₃CH₂)₄N] Mn_{1,5} Cl₃ 4H₂O Cl 2(H₂O) in the plan (a,b) shows an arrangement in layers perpendicular to the direction b. The structure consists of infinite parallel two-dimensional planes built connected ions and water molecules by strong O-H...O and O-H...Cl hydrogen bonding.

Keywords: Hybrid compound; X-ray diffraction; Infrared spectroscopy; Raman spectroscopy

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1. Introduction

The combination of organic molecules and inorganic materials was the starting point for the development of new hybrid compounds, with expected physical and chemical properties. These compounds have attracted great attention because of their unique opportunity to combine the remarkable features of organic compounds with those of inorganic materials. Their applications have been explored and reported in various fields, such as magnetism, conductive, luminescence and optics [1-5]. The materials based upon substituted complex ammoniums with halogenated metals such as Hg, Cd, Zn, Mn and Cu etc. present very interesting physical properties [6–12].

On the other hand, hybrid compounds based on tetra-alkylammonium cations of the general formula $(C_nH_{2n+1})_4N^+$ such as $(CH_3)_4N^+$, $(C_2H_{25})_4N^+$ and $(C_3H_7)_4N^+$ [10,12,13]. The specific geometry of these cations can generate supramolecular networks in one, two or three dimensions.

However, in conjunction with some resent works on these hybrids compounds, the crystal structure and vibrational studies of many organic-inorganic crystals have been investigated in our laboratory [14-16]. The present work deals with the growth, single X-ray diffraction (XRD) study and the detailed vibrational spectral analysis of a new organic-inorganic crystal: [($CH_3 CH_2$)_4N] Mn_{1,5} Cl_3 4H_2O Cl 2(H_2O).

2. Experiment

2.1. Synthesis

The title compound was prepared by mixing $(CH_3CH_2)_4NOH$ (1 mmol), $MnCl_2$. (2 mmol), concentrated HCl (1 mL) and water (10 mL). The mixture was then allowed to stand and evaporate slowly at room temperature. After 3 days, pink crystals appeared and they were studied by single crystal X-ray diffraction. The analysis of the obtained phase confirms the formation of $[(CH_3CH_2)_4N]$ $Mn_{1,5}$ Cl_3 $4H_2O$ Cl $2(H_2O)$.

2. 2. X-ray collection

Single-crystal X-ray data of $[(CH_3 CH_2)_4N]$ Mn_{1,5} Cl₃ 4H₂O Cl 2(H₂O) were collected at room temperature on a Nonius Kappa-CCD diffractometer using Mo-K α radiation ($\lambda = 0.71073$ Å) through the program COLLECT [17]. Correction for Lorentz-polarisation effect, peak integration and background determination were carried out with the program DENZO [18]. Frame scaling and unit cell parameters refinement were performed with the program SCALEPACK [18].

Pertinent details of the crystal structure of [(CH₃ CH₂)₄N] Mn_{1,5} Cl₃ 4H₂O Cl 2(H₂O) are listed in Table 1. The crystal

structure has been solved and refined in the triclinic symmetry, space group P1, using the WINGX environment [19] and based on SHELXS97 [20] and SHELXL97 [21] softwares. All the hydrogen positions of the diprotonated cation were placed geometrically and held in the riding mode the C–H bonds were fixed and O…H were affined at 0.96 to 0.97 Å and 0.73(8) to 0.95(8) Å, respectively). Bond distances and angles calculated from the final atomic coordinates, as well as probable hydrogen bonds, are given in Tables 2, 3 and 4 respectively.

2. 3. Spectroscopic measurements

The Fourier transform infrared (FT-IR) spectrum of the title compound was recorded in the range 4000-400 cm⁻¹, with samples in KBr pellets using PERKIN-ELMER FT-IR spectrometer. The resolution of the spectrum is ± 2 cm⁻¹. The Fourier transform Raman (FT-Raman) spectrum of the same compound was recorded using Horiba Jobin Yvon LabRAM HR 800 Dual Spectrophotometer. The incident laser excitation is 632 nm. The scattered light was collected at the angle of 180° in the region 3600-50 cm⁻¹ and the resolution was set up to 2 cm⁻¹.

3. Results and discussion

3.1 Refinement of the structure

The structure of this compound was solved in the triclinic space group P-1, which consists of anionic chains of singly edge-sharing manganese (II) metal centers through chloride atoms. The asymmetric unit (Fig. 1) consists of a single Mn(1) Cl 2H₂O moiety, Mn(2) Cl₂ 2H₂O moiety, two water molecules 2H₂O, a chloride anion Cl and tetraethylammonium [(C_2H_5)₄N] cation, which under the appropriate symmetry operations yields a molecular structure as shown in figure 2.

The first octahedral Mn(1) metal center lying in a special position, are coordinated by two chloride atoms symmetry [Cl5, Cl5^a; (a) -x, -y+2, -z] and four corners of water molecules (Mn-O vary from 2.205(1) to 2.241 (2)) forming a distorted octahedra geometry (Table 2).

The Monomers octahedral $Mn(1)Cl_2 2H_2O$ are located on planes perpendicular to the b axis at z = 0. Between two successive inorganic layers are interposed a free chlorine atom CI (6) and two water molecules.

The second octahedral Mn(2) metal center is in a general position, it is achieved by means of four bridging chloride atoms, two terminals of H_2O molecules. The shortest Mn...Mn distance in the molecule chain is 3.733 Å. The bridging Mn–Cl distances, which are in the range from 2.545 (4) to 2.574 (4)Å [22], and the Mn-O distances are in the range from 2.164 (2) to 2.173 (2) (Table 2).

The Octahedral polymers formed by the association of monomers $[Mn(2) Cl_2 (H_2O)_2]$ are linked through two chlorine atoms giving rise to an infinite chain of formula $[Mn (2) Cl_2 2H_2O]_n$. These chains are developed along the a axis at $z = \frac{1}{2}$.



The [Mn(2)Cl₂ (2H₂O)]n linear chains and the [Mn(1)Cl (2H₂O)] isolated octahedron are interconnected of hydrogen bonds by type O-H...Cl and also by the water molecules of two types of hydrogen bonds (table 4) : O-H...O, O-H...Cl as illustrated in figure 3. The lengths of the N-C bonds are in the range between 1.510(5) and 1.526(5)Å. The C-N-C angles range from 106.1(3) to 111.4(3)°. The C-C bonds lengths are in the region between 1.510(6) and 1.520(5).

Table. 1. Procedures for data collection and refinement of

[(CH₃ CH₂)₄N] Mn_{1,5} Cl₃ 4H₂O Cl 2(H₂O)

Compound	[(CH ₃ CH ₂) ₄ N] Mn _{1,5} Cl ₃ 4(H ₂ O) Cl 2(H ₂ O)
Habit-colour	Plate- pink
Density	1,55
Crystal system	Triclinic
Space group	P-1
z	1
α (Å)	7.542(4)
p (Á)	9.846(4)
c (Á)	13.767(6)
a(°)	89.951(3)
β (°)	89.753(3)
γ(°)	81.861(3)
Standard reflections	7320
Reflections with I > 2σ (I)	3548
T min	0,3736
T max	0,9290
R	0,055



Table. 2. Main interatomic distances and bond angles obtained for [(CH₃ CH₂)₄N] Mn_{1,5} Cl₃ 4H₂O Cl 2(H₂O)

Distances (Å)		Angles (°)
Mn(1)-Cl(5)	2.4862(9)	O(6)-Mn(1)-O(6) ⁱ 180.0
Mn(1)-O(5)	2.2415(12)	O(6)-Mn(1)-O(5) ⁱ 92.5
Mn(1)-O(6)	2.2030(12)	O(6) ⁱ⁻ Mn(1)-O(5) _i 87.5
Mn(2)-Cl(4) ⁱⁱ	2.5453(10)	O(6) ⁱ⁻ Mn(1)-O(5) 92.5
Mn(2)-Cl(3) ⁱⁱⁱ	2.5670(10)	O(5) ⁱ -Mn(1)-O(5) 180.00(6)
Mn(2)-O(1)	2.1644(13)	O(6)-Mn(1)-Cl(5) 90.89(4)
Mn(2)-O(2)	2.1734(13)	O(6) ⁱ -Mn(1)-Cl(5) 89.11(4)
Mn(2)-Cl(3)	2.5725(10)	O(5) ⁱ⁻ Mn(1)-Cl(5) 91.27(4)
Mn(2)-Cl(4)	2.5745(10)	O(5)-Mn(1)-Cl(5) 88.73(4)
		O(6) ⁱ -Mn(1)-Cl(5) ⁱ 90.89(4)
		O(5)-Mn(1)-Cl(5) 88.73(4)
		O(5)-Mn(1)-Cl(5) ⁱ 91.27(4)
		O(1)-Mn(2)-O(2) 178.65(7)
	1	O(1)-Mn(2)-Cl(4) ⁱⁱ 86.57(4)
		O(2)-Mn(2)-Cl(4) ⁱⁱ 92.11(4)
		O(1)-Mn(2)-Cl(3) ⁱⁱⁱ 87.56(4)
		O(2)-Mn(2)-Cl(3) ⁱⁱⁱ 93.76(4)
		CI(4) ⁱⁱ -Mn(2)-CI(3) ⁱⁱⁱ 174.05(4)
		O(1)-Mn(2)-Cl(3) 94.87(4)
		O(2)-Mn(2)-Cl(3) 85.57(4)
		CI(4) ⁱⁱ⁻ Mn(2)-CI(3) 97.22(3)
		CI(3) ⁱⁱⁱ -Mn(2)-CI(3) 84.23(3)





O(1)-Mn(2)-Cl(4)	94.03(4)
O(2)-Mn(2)-Cl(4)	85.61(4)
Cl(4) ⁱⁱ -Mn(2)-Cl(4)	86.38(3)
CI(3) ⁱⁱⁱ -Mn(2)-CI(4)	93.08(3)
CI(3)-Mn(2)-CI(4)	170.59(4)

Symmetry codes:

(I)-x, -y+2, -z;

(II) -x -y, -z+1;

(III) -x+1, -y, -z+1

	Distances (Å)	Ang	gles (°)
N(1)-C(1)	1.526(5)	C(2)-N(1)-C(3)	111.3(3)
N(1)-C(2)	1.510(5)	C(2)-N(1)-C(4)	111.4(3)
N(1)-C(3)	1.516(5)	C(3)-N(1)-C(4)	107.2(3)
N(1)-C(4)	1.519 <mark>(</mark> 5)	C(2)-N(1)-C(1)	106.1(3)
C(1)-C(6)	1.513(6)	C(3)-N(1)-C(1)	110.5(3)
C(2)-C(8)	1.515(5)	C(4)-N(1)-C(1)	110.3(3)
C(3)-C(7)	1.521(4)	N(1)-C(2)-C(8)	113.7(3)
C(4)-C(5)	1.511(6)	N(1)-C(3)-C(7)	115.3(3)
		C(6)-C(1)-N(1)	115.1(3)
		C(5)-C(4)-N(1)	114.6(3)

Table. 3. Final atomic coordination, Ueq and temperature factors (Uiso for H atoms) of

[(CH₃ CH₂)₄N] Mn_{1,5} Cl₃ 4H₂O Cl 2(H₂O)

Atomes	x/a	y/b	z/c	U _{eq} et U _{iso⁺}
Mn(1)	0.0000	1.0000	0.0000	0.0265(2)
Mn(2)	0.2468(6)	0.0028(5)	0.4968(4)	0.0261(2)
Cl(3)	0.4726(11)	0.1740(9)	0.4780(7)	0.0325(2)
CI(4)	0.0331(11)	-0.1678(9)	0.54558(7)	0.0310(2)
CI(5)	-0.0149(13)	1.0439(11)	0.1778(6)	0.0393(3)
CI(6)	0.5396(12)	0.8165(10)	0.1884(7)	0.0355(2)
O(1)	0.2559(2)	-0.0565(12)	0.3454(8)	0.0519(9)
O(2)	0.23139(2)	0.0650(12)	0.6484(8)	0.0373(7)
O(3)	0.6282(2)	0.2503(12)	0.2673(8)	0.0493(8)
O(4)	0.4713(2)	0.1309(12)	0.1146(8)	0.0485(7)
O(5)	0.1747(2)	1.1650(12)	-0.0149(8)	0.0379(6)
O(6)	0.2469(2)	0.8534(12)	0.0176(8)	0.0379(6)
N	-0.0991(4)	0.4848(3)	0.7481(2)	0.0275(6)
C(1)	-0.2321(6)	0.5515(4)	0.6729(3)	0.0400(9)
C(2)	-0.0157(6)	0.6002(4)	0.7933(3)	0.0432(10)
C(3)	-0.1940(6)	0.4088(4)	0.8236(3)	0.0408(9)
C(4)	0.0413(6)	0.3804(4)	0.6998(3)	0.0421(10)
C(5)	0.1552(7)	0.4395(5)	0.6246(4)	0.0538(12)
C(6)	-0.3340(7)	0.4535(5)	0.6190(4)	0.0544(12)
C(7)	-0.3410(2)	0.4965(12)	0.8805(8)	0.0552(12)
C(8)	0.1230(2)	0.5528(12)	0.8699(8)	0.0639(14)
H1A	-0.1676	0.5995	0.6259	0.048
H1B	-0.3178	0.6195	0.7054	0.048
H2A	-0.1096	0.6650	0.8225	0.052
H2B	0.0402	0.6480	0.7425	0.052
НЗА	-0.2458	0.3363	0.7914	0.049
НЗВ	-0.1056	0.3657	0.8692	0.049
H4A	0.1192	0.3354	0.7496	0.050
H4B	-0.0186	0.3109	0.6690	0.050
H5A	0.2401	0.3674	0.5976	0.081
H5B	0.2179	0.5067	0.6545	0.081
H5C	0.0799	0.4820	0.5738	0.081
H6A	-0.4141	0.5039	0.5735	0.082
H6B	-0.4016	0.4073	0.6645	0.082
H6C	-0.2511	0.3872	0.5848	0.082
H7A	-0.3931	0.4402	0.9265	0.083
H7B	-0.4317	0.5375	0.8366	0.083
H7C	-0.2911	0.5674	0.9144	0.083



H8A	0.0683	0.5074	0.9213	0.096
H8B	0.2183	0.4905	0.8413	0.096
H8C	0.1705	0.6308	0.8957	0.096
H1A	0.3406	-0.0934	0.3178	0.047(2)
H2A	0.3152	0.1032	0.6798	0.050(2)
НЗА	0.7481	0.2017	0.2565	0.10(2)
НЗВ	0.5766	0.2427	0.3140	0.10(2)
H4A	0.5061	0.1853	0.1654	0.050(2)
H4B	0.4900	0.0567	0.1297	0.050(2)
H5A	0.2445	1.1816	0.0299	0.09(2)
H5B	0.2409	1.1633	-0.0775	0.13(3)
H6A	0.3126	0.8561	0.0725	0.059(2)
H6B	0.3306	0.8490	-0.0210	0.050(2)

Table.4. Bond lengths (Å) and bond angles (°) in the hydrogen bonding scheme of $[(CH_3 CH_2)_4N] Mn_{1,5} Cl_3 4H_2O CI 2(H_2O)$

D-HA	d(D-H) (Å)	d(HA) (Å)	d(DA) (Å)	∠ D-HA (°)
O1-H1ACl6	0.78	2.41	3.165(15)	161.3
O1-H1BCl5	0.94	2.33	3.152(14)	146.3
O2-H2ACI6"	0.89	2.32	3.161(14)	157.2
O2-H2BCl5 [™]	0.77	2.41	3.161(15)	165.2
03-H3ACI5 ^{IV}	0.97	2.45	3.364(15)	157.5
O3-H3BCl3 ^v	0.76	2.51	3.251(15)	165.6
04-H4A03 ^v	0.94	1.85	2.761	163.3
O4-H4BCl6	0.75	2.48	3.229(15)	176.4
O5-H5AO4'	0.84	2.08	2.850	152.1
05-H5BCl6 ^{vi}	0.99	2.28	3.231(14)	161.2
O6-H6ACl6	0.91	2.34	3.216 (14)	163.2
06-H6B04 ^{vii}	0.82	2.00	2.813(2)	171.3

Symmetry codes:

- (i) x, y−1, z;
- (ii) -x+1, -y+1, z
- (iii) -x, -y+1, -z+1;
- (iv) x+1, -y+1, z;
- (v) x, y, z;
- (vi) -x+1, -y+2, -z;
- (vii) -x+1, -y+1, -z.



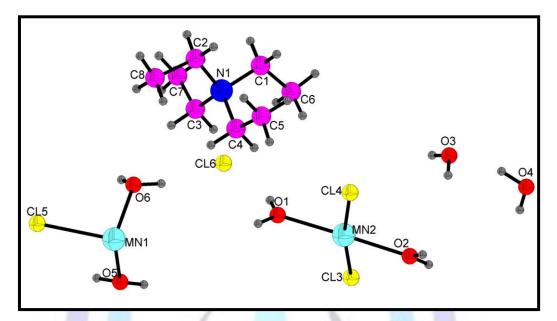


Figure. 1. The asymmetric unit of [(CH₃ CH₂)₄N] Mn_{1,5} Cl₃ 4H₂O Cl 2(H₂O)

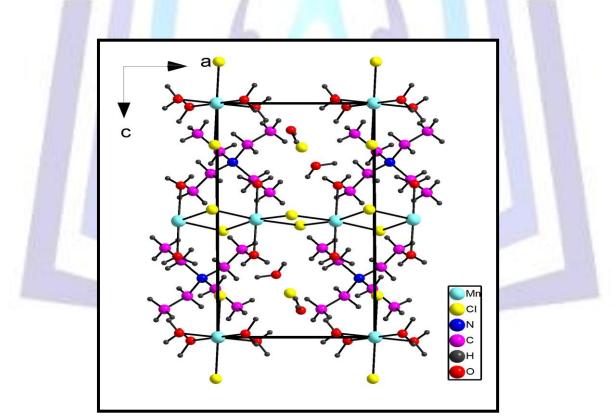


Figure. 2. Projection along the b axis of the atomic arrangement of [(CH₃ CH₂)₄N] Mn_{1,5} Cl₃ 4H₂O Cl 2(H₂O)



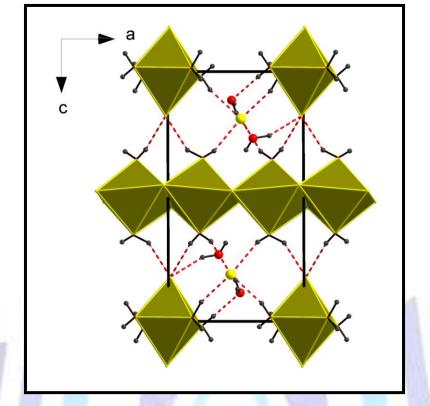


Figure. 3. Projection along the b axis of the inorganic arrangement of [(CH₃ CH₂)₄N] Mn_{1.5} Cl₃ 4H₂O Cl 2(H₂O)

3. 2. Vibrational analysis

3. 2. 1. The tetraethylammonium cation vibrations

Numerous functional and skeletal groups such as CH₂, CH₃, N-C, C-C, NC₄ are present in tetraethylammonium cation. These groups are manifested in IR and Raman spectra in different range with different intensity are given in Figs 4,5.

*Methyl vibrations

The asymmetric and symmetric CH_3 stretching vibrations are usually observed in the region 3000-2850 cm⁻¹ [23]. The weak band at 3003 cm⁻¹ in IR spectrum is attributed to the asymmetric stretching V_{as} (CH₃) vibration. The Raman counterpart is located as a very strong band at 2998 cm⁻¹. The symmetric stretching mode V_{as} (CH₃) is observed as shoulder band at 2897 cm⁻¹ in Raman spectrum. In IR spectrum this mode appears as a very weak intensity band at the 2965 cm⁻¹. The asymmetric and symmetric bending mode of methyl group generally appears in the region 1550-1410 and 1400-1340 cm⁻¹ respectively. In the present case, the medium IR band at 1494 cm⁻¹ is assigned to CH₃ asymmetric bending mode

 δ_s (CH₃) is located at 1402 cm⁻¹ as a weak band in the IR spectrum and as a very weak band at 1387 cm⁻¹ in Raman spectrum. The methyl rocking vibration is observed as a weak band at 997 cm⁻¹ in IR spectrum and at 1001 cm⁻¹ as a medium one in Raman spectrum.

*Methylene group vibrations

The wavenumber of the CH_2 vibrational modes depend on its immediate environment. The stretching modes of the CH_2 group usually occur in the region 3100-2800 cm⁻¹ [24]. In the title compound, the CH_2 asymmetric and symmetric stretching modes are observed in Raman spectrum at 2946 cm⁻¹ as very strong band and at 2824 cm⁻¹ as very weak band respectively. In IR spectrum, these modes are probably masked by the broad band around 2900 cm⁻¹. The wagging, twisting and the rocking modes of the CH_2 group were observed and assigned.

*NC₄ group vibrations

The primitive unit cell of the title compound contains one tetrapropylammonium $(NC_4)^+$ cation not coupled with the inorganic parts as revealed by the X-Ray diffraction. Then, it is convenient as a first approach to consider the NC₄ core of the isolated cation with Td symmetry and therefore exhibits four normal modes. According to the literature, the vibrations related to NC₄ group shown in tetrapropylammonium cation are described as: symmetric stretching mode v₁(A) to be



found at 752 cm⁻¹, asymmetric stretching mode V_3 (F₂) located at 955 cm⁻¹, asymmetric bending mode V_4 (F₂) observed at 455 cm⁻¹ and the symmetric bending mode V_2 (F₂) at 372 cm⁻¹ [25-26]. In our case the very weak Raman band appeared at 1044 cm⁻¹ is related to the V_3 mode. His counterpart appears in IR spectrum as weak band at 1011 cm⁻¹. The week band observed in Raman spectrum at 787 cm⁻¹ and the shoulder one at 790 cm⁻¹ in IR spectrum arises from the symmetric stretching mode $v_1(NC_4)$. The band assigned to the symmetric bending modes of NC₄ core of the isolated cation is observed in Raman spectrum at 325 cm⁻¹ with no conteroart in IR spectrum. The asymmetric band $v_2(NC_4)$ is not observed in IR spectrum and probably masked by the very intense band at 417 cm⁻¹ assigned in Raman spectrum. It is interest to note that the vibrational mode of the NC₄ group do not deviate much from their expected values, suggesting that the interaction of this group with the environment is not strong. On the other hand, we note that our assignment of NC₄ agree well with the previous reported vibrational studies of the tetrapropylammonium salts [27].

*N-C, C-C, C-C-C and C-C-N group of vibrations

The absorption bands arising from N-C symmetric stretching vibrations are observed in the wavenumber region 850-1150 cm⁻¹. In the present crystal the strong Raman band at 1117 cm⁻¹ is assigned to this mode. His IR counterpart is identified at 1174cm⁻¹. The corresponding theoretical value is at 1127 cm⁻¹. The absorption bands arising from the C-N-C stretching mode is observed in IR spectrum at 1011cm⁻¹ and in Raman spectrum at 1117, 745 and 676 cm⁻¹. The weak bands appeared at 1150 and 1146 cm⁻¹ in IR spectrum and at 1173 and 1151 cm⁻¹ in Raman are related to C-C stretching mode. The C-C-C vibrational bands have been identified and assigned. Table 5 presented a detailed assignment of all observed band related to organic cation.

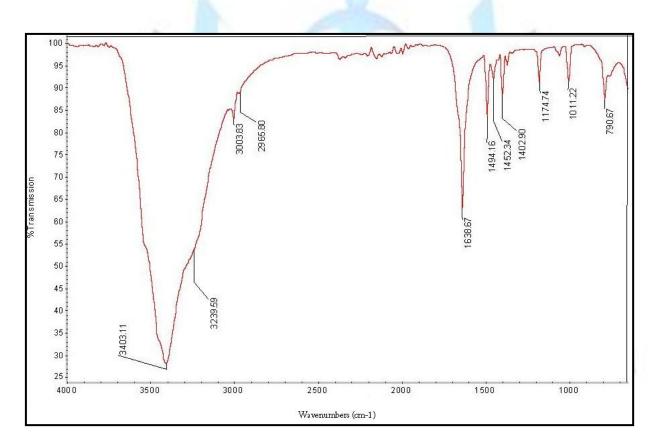
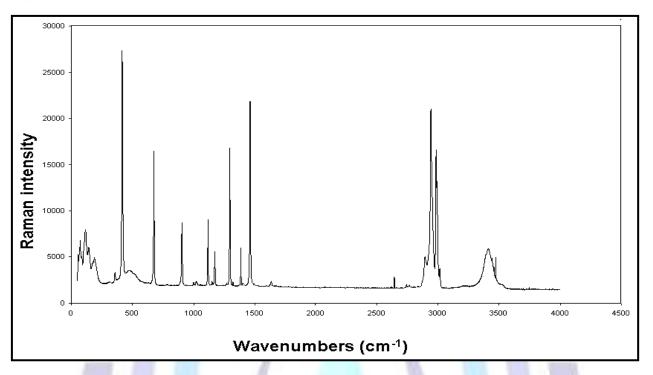


Figure.4. IR spectrum of [(CH₃ CH₂)₄N] Mn_{1,5} Cl₃ 4H₂O Cl 2(H₂O)







4. Summary

Crystals of a hybrid material, $[(CH_3 CH_2)_4N]$ Mn_{1,5} Cl₃ 4H₂O Cl 2(H₂O), have been prepared by slow evaporation of aqueous solution (CH₃CH₂)₄NOH, MnCl₂. and concentrated HCl at room temperature and characterized by means of single-crystal X-ray diffraction, FT-IR and Raman vibrational study. The structure consists of strong two dimensional character based on sheets of [Mn(2)Cl₂ (2H₂O)]n and [Mn(1)Cl (2H₂O)] are interconnected of hydrogen bonds by type O-H...Cl and also by the water molecules of two types of hydrogen bond O-H...O, O-H...Cl. The planes of inorganic groups alternated with planes of the organic cations.

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