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Synthesis, Crystal Growth, Structure, Spectral, Optical and Thermal Characterization of M-Toluidinium Picrate Single Crystal

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Abstract: A new charge transfer molecular complex salt of picric acid with m-toluidine was synthesized and the structure confirmed by single crystal X-ray diffraction (XRD) and NMR spectral analyses. Single crystals of m-toluidinium picrate have been grown by slow solvent evaporation solution growth technique using ethanol as the solvent at ambient temperature. The single crystal XRD analysis of MTP salt confirms the formation of 1:1 charge transfer salt in which the constituent ions are held together by strong intermolecular N^+-H-O^- type hydrogen bonds. The title compound crystallizes in monoclinic crystal system with centrosymmetric space group $P2_1/c$. The optical properties were studied by the UV-Vis-NIR transmittance and the fluorescence emission studies. Fourier transform infrared (FT IR) spectral analysis was used to confirm the presence of various functional groups in the grown crystal. Thermal stability of the grown MTP crystal was established using the thermo gravimetric and differential thermal analysis.

Keywords: Nonlinear optical; Single crystal; Characterization; X-ray diffraction.

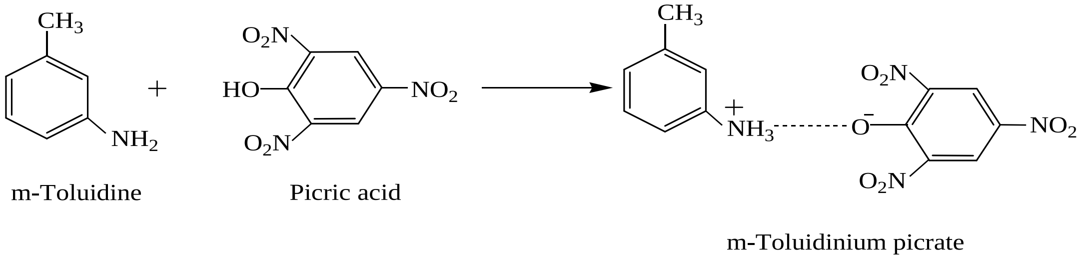
1. Introduction

The crystal engineering has its roots in the field of the design and synthesis of crystalline materials of the soild-state organic chemistry[1-2]. Molecular flexibility of organic materials also paves the way to enhance the nonlinear optical (NLO) properties in a desired manner[3]. Mulliken suggested that the charge transfer interactions from two aromatic molecules can arise from the transfer of an electron from Lewis base to Lewis acid. Generally, proton transfer interactions between electron donor and electron acceptor molecules leads to the formation of intensely colored charge transfer complexes[4-5]. The non-linear optical properties of many of the molecular organic crystals are due to the presence of delocalized π-electron systems linking donor and acceptor groups which enhance the necessary asymmetric polarizability. The charge transfer complexes are currently of great importance since these materials can be utilized for having non-linear optical property and electrical conductivities[6-12]. Picric acid, as a proton donor forms crystalline picrates of various organic molecules by virtue of its lewis acid behavior and serves a better acidic ligand in the formation of salts through specific electrostatic or hydrogen bonding interactions[13]. The charge transfer transition in the picrate complexes depends on the nature of the partners involved in the bond-formation process[14]. Picric acid derivatives are interesting candidates, as the presence of an activating phenolic OH and electron withdrawing nitro groups favors the formation of salts with various organic bases such as N,N-dimethylanilinium picrate[15], 3-Methyl aniliniumpicrate[16], 2-Chloroanilinium picrate[17], Anilinium picrate[18], p-toluidinium picrate[19,20], 8-hydroxyquinolinium picrate[21], 1,3-Dimethylurea dimethyl ammonium picrate[22] have already been reported. Research in this direction led to the successful synthesis of the charge transfer complex salt m-toluidinium picrate (MTP), which crystallizes in the monoclinic crystal system with centrosymmetric space group $P2_1/c$ and was characterized by various spectral, optical and thermal studies.

2. Experimental Procedure

2.1. Material Synthesis:

AnalaR grade of picric acid, m-Toluidine, were used for the synthesis of the title salt. m-Toluidine (1.07 g, 0.01 mol) was dissolved in 15 ml of ethanol. Picric acid (2.29 g, 0.01 mol) was dissolved in 30 ml of ethanol. Both the solutions were mixed together and stirred well for about an hour. The yellow colored precipitate of the charge transfer complex salt MTP was obtained due to the proton transfer from the –OH group of picric acid to the amino group of m-toluidine. The precipitate was then filtered off and dried and repeatedly recrystallized from pure and distilled ethanol to enhance the degree of the purity of the salt. The reaction involved in the synthesis of MTP is illustrated in the following equation



2.2. Growth of single crystals

A saturated solution of the charge transfer salt, MTP was prepared in ethanol and stirred well for about two hours. Then, the solution was filtered through a quantitative Whatmann 41 grade filter paper to eliminate the suspended impurities present in the solution. The clear filtrate thus obtained was kept aside unperturbed in an atmosphere most suitable for the growth of the single crystals. In about a week time, good optical quality yellow colored single crystals of the title salt were harvested. The photograph of the as-grown crystals of the salt of MTP is depicted in Fig. 1.

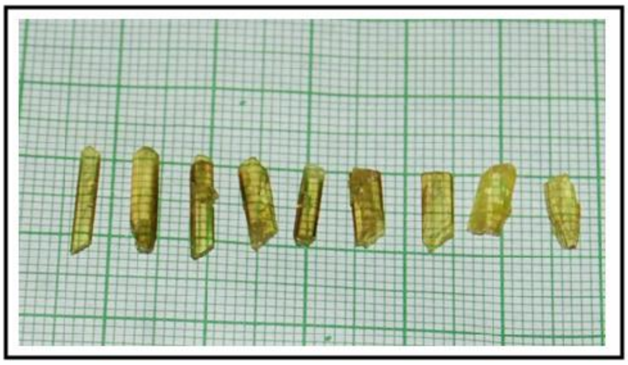


Fig. 1. As-grown single crystals of MTP

2.3. Characterization techniques

The grown MTP crystal was subjected to various characterization techniques like ^{1}H and ^{13}C NMR spectral analyses, single crystal X-ray diffraction, Fourier transform infrared (FT IR), UV-Vis-NIR spectral analysis, thermal analyses and fluorescence emission studies. The ^{1}H NMR and ^{13}C NMR spectra of MTP crystals were recorded employing the 'BRUKER AVANCE III 500 MHz (AV 500) spectrometer with TMS as the internal reference standard and DMSO as the solvent. The functional groups of MTP crystal are confirmed by recording the fourier transform infrared (FT-IR) spectrum in the range of 4000-400 cm^{-1} using Perkin-Elmer FT-IR spectrometer by the KBr pellet technique. Single crystal XRD analysis for the grown m-toluidinium picrate crystal has been carried out to identify the unit cell parameters and the crystal structure using 'ENRAF(BRUKER) NONIUS CAD4' diffractometer with graphite monochromated MoKα radiation (λ=0.71073 Å). The structure was solved by direct methods procedure as implemented in SHELXS 97[23] program. Cell refinement and data reduction were carried out using SAINT program. All the hydrogen atoms were fixed geometrically and allowed to ride on their parent atoms. All non-hydrogen atoms were refined using anisotropic displacement parameters. The optical transmission spectrum of MTP crystals were recorded in the range 200-1100 nm employing a Shimadzu UV-1061 UV-Vis spectrophotometer in the solution using DMSO as the solvent. The fluorescence emission spectrum of MTP was recorded using HORIBA JASCO V-670 FLUOROLOG 3 spectrofluorometer. The thermal stability of MTP was established by thermo gravimetric (TG) and differential thermal analyses (DTA) using STA 409 PL LUXX analyser. The sample was analyzed between the temperatures 26 and 500°C at a heating rate of 10K/min in nitrogen atmosphere.

3. Results and Discussions

3.1. Nuclear magnetic resonance studies

In the ^{1}H NMR spectrum (Fig. 2) of MTP, the appearance of five proton signals indicates the presence of five different proton environments in the MTP crystal. The broad hump at δ 9.75 ppm confirms the presence of highly deshielded $^{+}NH_3$ protons of m-toluidinium moiety. The singlet peak at δ 8.61 ppm is assigned to the C3 and C5 aromatic protons of the same kind in picrate moiety. The triplet signal centered at δ 7.36 ppm has been assigned to the C5 aromatic proton of m-toluidinium moiety. The multiplet signal centered at δ 7.21 ppm is due to the overlapping of a doublet attributed to C4 and C6 aromatic protons of the same kind and the other singlet due to C2 aromatic proton in m-toluidinium moiety. The signal corresponding to the three chemically and magnetically equivalent methyl protons of m-toluidinium moiety appears as an intense singlet at δ 2.33 ppm.

The ^{13}C NMR spectrum of MTP is depicted in Fig. 3. The appearance of ten distinct carbon signals in the spectrum establishes the molecular structure of the MTP complex. The weak signal appearing at δ 161.37 ppm has been assigned to the ipso carbon of the (C1) picrate moiety. The signal at δ 142.24 ppm is attributed to the C2 and C6 carbon atoms of the same kind in picrate moiety. The signal due to C3 and C5 carbon atoms of the same kind in picrate moiety appears as an intense signal at δ 125.72 ppm. The signal at δ 123.91 ppm owes to the C4 carbon atom of the same moiety in the complex. The C4 and C6 aromatic carbon atoms of m-toluidinium moiety collectively stand responsible for the carbon signal appearing at δ 130.07 ppm. The peaks appearing at δ 140.05, 132.02, 129.28 and 120.61 ppm have been assigned, respectively to C2, C5, C3 and C1 carbon atoms in m-toluidinium moiety in the salt. The methyl carbon of m-toluidinium moiety exhibits a signal at δ 21.20 ppm.

3.2. Fourier transform infrared spectroscopy

The FT-IR spectrum of MTP crystal is shown in Fig. 4. and the assignments of the various bands are given in Table.1. The formation of the charge transfer complex of m-toluidinium picrate is strongly evidenced by the presence of the main characteristic infrared bands of the donor and acceptor in the spectrum of MTP salt with slight changes in frequencies. The band at 3186 cm^{-1} is due to the ^{+}N-H asymmetric stretching vibration. The absorption bands at 3075 and 2927 cm^{-1} have been assigned to the asymmetric and symmetric aromatic C-H stretching vibrations respectively. The band due to C-H asymmetric stretching vibration of methyl group almost overlaps with aromatic C-H symmetric stretching vibrations. The symmetric C-H stretching vibration of methyl group has been observed at 2851 cm^{-1}. Like other aromatic nitro compounds m-toluidinium picrate also exhibits the absorption bands due to the asymmetric and symmetric stretching vibrations of the $-NO_2$ group at 1534 and

1325 cm^{-1} respectively. The bands at 1570, 1612 and 1430 cm^{-1} are attributed to the C=C aromatic stretching vibrations. The C-H inplane bending vibration has been observed at 1163 cm^{-1}. The C-O stretching vibration is observed at 1275 cm^{-1}. These assignments are in good agreement with the data already reported for a number of related charge transfer complex salts[8-11].

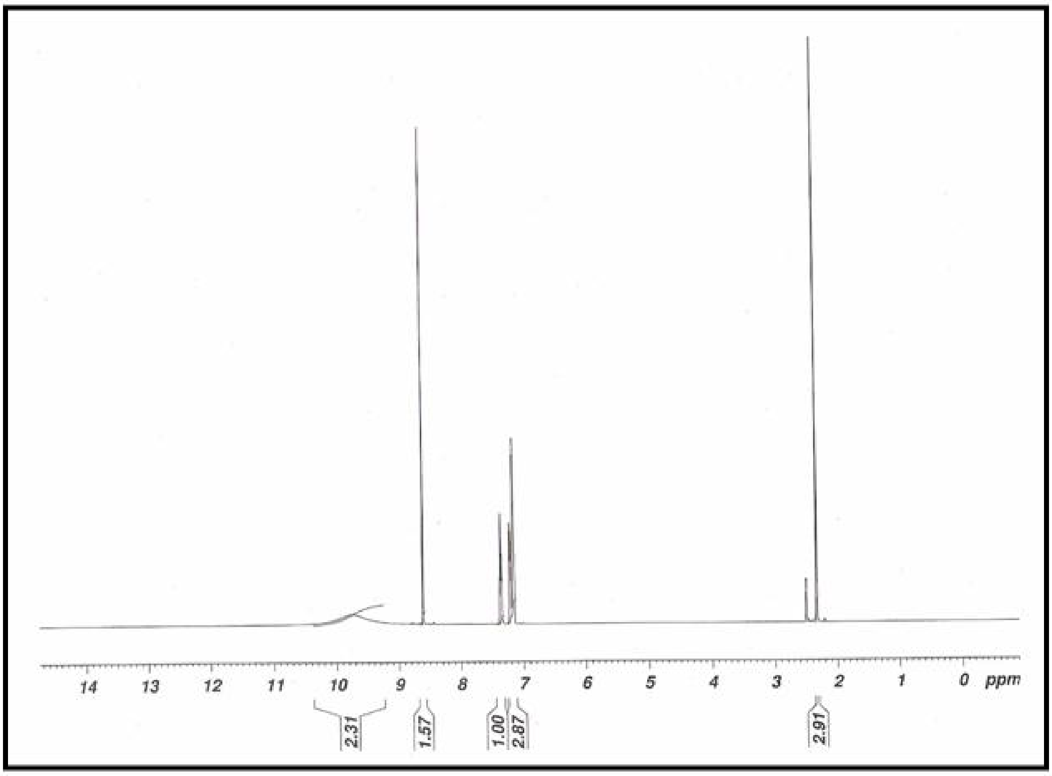


Fig. 2. ^{1}H NMR spectrum of MTP

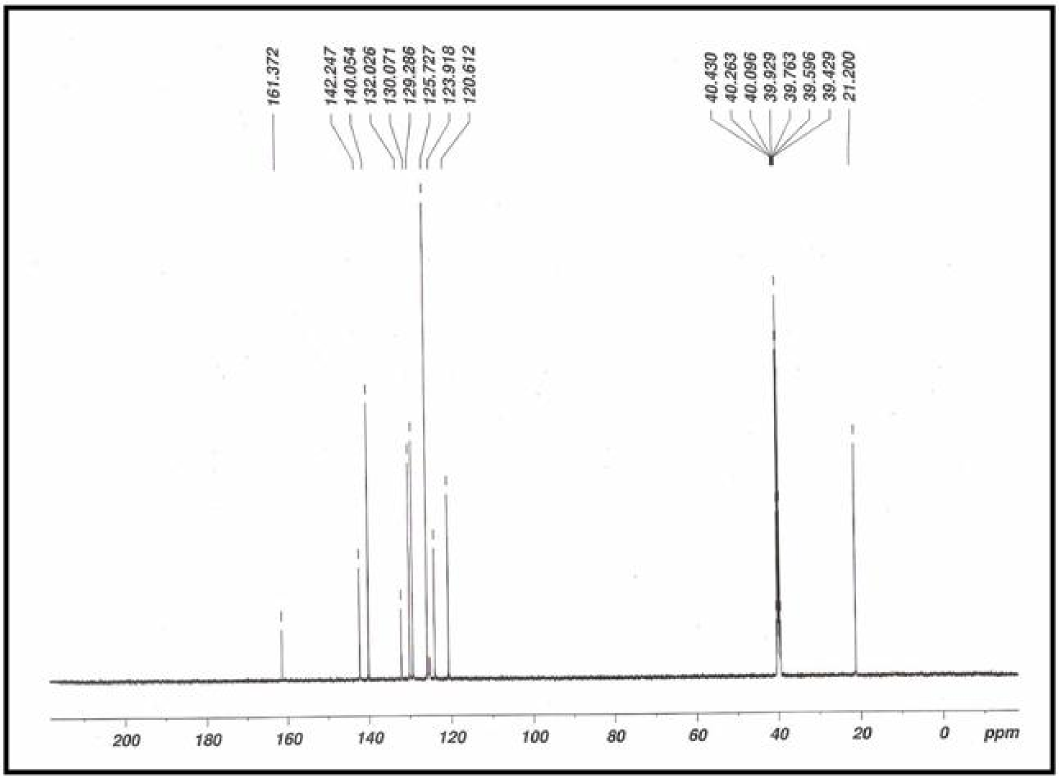


Fig. 3. ^{13}C NMR spectrum of MTP

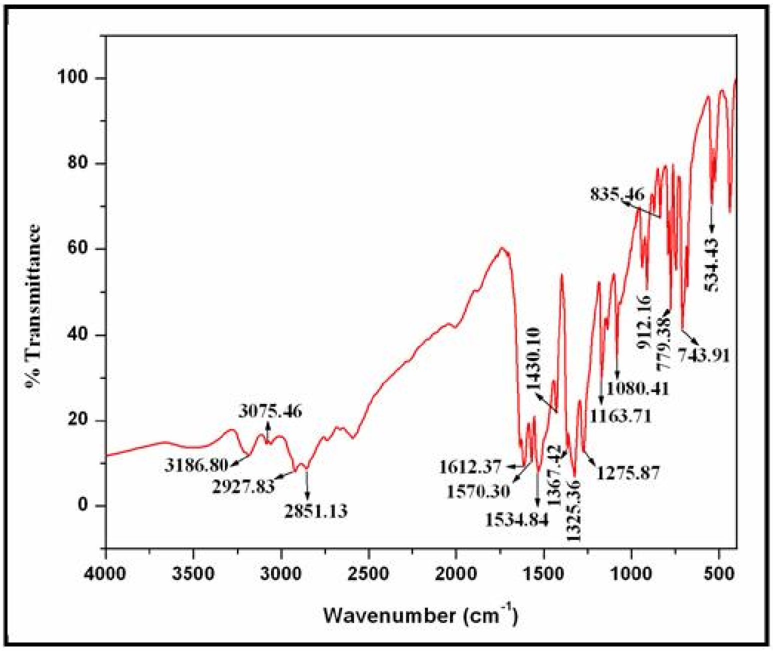


Fig. 4. FT-IR Spectrum of MTP

Table. 1. FT-IR frequency assignment for MTP

Observed frequency (in cm^{-1})	Assignment
3186	$^{+}$N-H stretching
3075	Aromatic C-H asymmetric stretching
2927	C-H asymmetric stretching of methyl group/aromatic symmetric C-H stretching
2851	Symmetric C-H stretching vibration of methyl group
1612, 1570 & 1430	C=C aromatic stretching
1534	$-NO_2$ asymmetric stretching
1325	$-NO_2$ symmetric stretching
1275	C-O stretching vibration
1163,1080	C-H inplane bending vibration
912	$C-NO_2$ stretching
835	NO_2 scissoring
779	C-H bending (out of plane)
743	NO_2 wagging
534	NO_2 scissoring

3.3. Single crystal X-ray diffraction studies

Single crystal XRD analysis of MTP reveals that the title salt crystal crystallizes in a monoclinic crystal system with centrosymmetric space group $P2_1/c$ and the unit cell parameters are a=12.3595(5) Å, b=16.9012(6) Å, c= 7.4301(3) Å. Table. 2 summarize the crystal data, intensity data collection and refinement details for the MTP single crystals. The selected bond lengths and bond angles of MTP charge transfer complex salt are given in Table. 3 and Table. 4 respectively. The protonation on the N1 site of the cation is confirmed from C-N bond distances and C-N-C bond angles. All the bond distances and bond angles of the two molecules in the asymmetric unit agreed with each other. The formation of charge transfer complex depends on the nature of the donor-acceptor system and the orientation of anionic and cationic species which facilitates the formation of expected N-H·····O hydrogen bonds between amino hydrogen and phenolic oxygen[24].

Table. 2. Crystallographic data for MTP

Empirical formula	$C_{13}H_{12}N_4O_7$
Formula weight	336.27
Temperature	293(2) k
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	a=12.3595(5) Å, α=90° b=16.9012(6) Å, β=106.309(2)° c=7.4301(3) Å, γ=90°
Volume	1489.62(10)Å^3
Z, Calculated density	4, 1.499 Mg/m^3
Absorption coefficient	0.124 mm^{-1}
F(000)	696
Crystal size	0.30×0.20×0.20 mm
Theta range for data collection	2.10 to 24.99°
Limiting indices	-14<=h<=14, -19<=k<=20, -8<=1<=7
Reflections collected/unique	13502/2617 [R(int)=0.0243]
Completeness to theta=24.99	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9924 and 0.9315
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2617/12/250
Goodness-of-fit on F^2	1.013
Final R indices [I>2sigma(I)]	R1=0.0399, wR2=0.1138
R indices (all data)	R1=0.0484, wR2=0.1244
Extinction coefficient	0.019(2)
Largest diff. peak and hole	0.352 and -0.233 e.Å^{-3}

Table. 3. Selected bond lengths in MTP(Å)

C(1)—C(2)	1.369(3)
C(1)—C(6)	1.427(2)
C(1)—N(1)	1.457(2)
C(2)—C(3)	1.377(3)
C(2)—H(2)	0.9300
C(3)—C(4)	1.377(3)
C(3)—N(2)	1.443(2)
C(4)—C(5)	1.365(2)
C(4)—H(4)	0.9300
C(5)—C(6)	1.436(2)
C(5)—N(3)	1.453(2)
C(6)—O(7)	1.258(2)
C(7)—C(8)	1.371(3)
C(7)—C(12)	1.374(3)
C(7)—N(4)	1.460(2)
C(8)—C(9)	1.384(3)
C(9)—C(10)	1.365(4)

C(9)─C(13)	1.503(4)
C(10)─C(11)	1.370(4)
C(11)─C(12)	1.390(3)
N(1)─O(1)	1.177(6)
N(1)─O(2)	1.250(3)
N(2)─O(3)	1.217(2)
N(2)─O(4)	1.232(2)
N(3)─O(5)	1.218(2)
N(3)─O(6)	1.218(2)

Table. 4. Selected bond angles in MTP (°)

C(2)─C(1)─C(6)	124.27(16)
C(2)─C(1)─N(1)	116.27(16)
C(6)─C(1)─N(1)	119.43(15)
C(1)─C(2)─C(3)	118.85(17)
C(1)─C(2)─H(2)	120.6
C(2)─C(3)─C(4)	121.61(16)
C(2)─C(3)─N(2)	118.92(17)
C(4)─C(3)─N(2)	119.46(17)
C(5)─C(4)─C(3)	118.23(16)
C(3)─C(4)─H(4)	120.9
C(4)─C(5)─C(6)	124.84(16)
C(4)─C(5)─N(3)	117.12(15)
C(6)─C(5)─N(3)	118.02(14)
O(7)─C(6)─C(1)	125.24(16)
O(7)─C(6)─C(5)	122.70(15)
C(1)─C(6)─C(5)	112.06(14)
C(8)─C(7)─C(12)	122.12(18)
C(8)─C(7)─N(4)	118.38(16)
C(12)─C(7)─N(4)	119.48(18)
C(7)─C(8)─C(9)	120.31(19)
C(7)─C(8)─H(8)	119.8
C(10)─C(9)─C(8)	117.8(2)
C(10)─C(9)─C(13)	122.2(2)
C(8)─C(9)─C(13)	120.0(2)
C(9)─C(10)─C(11)	122.2(2)
C(10)─C(11)─C(12)	120.4(2)
C(7)─C(12)─C(11)	117.2(2)
O(1)─N(1)─O(2)	123.6(4)
O(1)─N(1)─C(1)	120.4(4)
O(2)─N(1)─C(1)	115.8(2)
O(3)─N(2)─O(4)	123.40(17)
O(3)─N(2)─C(3)	118.90(17)
O(4)─N(2)─C(3)	117.70(17)
O(6)─N(3)─O(5)	123.52(16)
O(6)─N(3)─C(5)	118.07(15)
O(5)─N(3)─C(5)	118.40(15)
H(4A)─N(4)─H(4B)	105.1(19)

Table. 5. Hydrogen bond parameters in MTP

D—H···A	d(D—H)	d(H···A)	d(D···A)	<(DHA)
N(4)—H(4A)···O(7)#1	0.88(3)	1.89(3)	2.749(2)	163(2)
N(4)—H(4A)···O(5)#1	0.88(3)	2.47(2)	2.970(2)	116.8(18)
N(4)—H(4B)···O(7)	0.98(2)	1.78(2)	2.758(2)	175(2)
N(4)—H(4B)···O(1)	0.98(2)	2.48(3)	2.977(16)	111.3(16)
N(4)—H(4C)···O(4)#2	0.94(3)	2.01(2)	2.887(2)	154.2(19)

#1 x,-y+1/2,z+1/2; #2 –x+1,y+1/2,-z+3/2

The crystallographic information file has been deposited by us in the Cambridge structure database **(CCDC 892444)**. These data can be obtained by free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data-request/cif.

A good optical quality yellow colored single crystal of MTP with dimension 0.30×0.20×0.20 mm was selected for diffraction analysis. A total of 13502 reflections (2617 Unique, R(int)=0.0243) were collected by using ù/2è scan mode at 293 K in the range of 2.10°<è<24.99° with the index ranges -14<=h<=14, -19<=k<=20, -8<=1<=7. The refinement converged to the final R-factor of 0.04 %. The residual electron density in the final difference fourier maps has maximum and minimum values of 0.352 and -0.233 e.Å^{-3}. The asymmetric part of m-toludinium picrate contains 3-methyl anilinium cation and picrate anion. Fig. 5. shows the ORTEP plot of the charge transfer complex salt MTP and the atom numbering scheme adopted. The carbon skeleton of the anionic picrate and cationic m-toluidinium moieties in charge transfer complex of MTP is non-planar as shown in the torsion angle of N(1)-C(1)-C(2)-C(3), N(2)-C(3)-C(4)-C(5), N(3)-C(5)-C(6)-C(1), N(4)-C(7)-C(8)-C(9), C(13)-C(9)-C(10)-C(11), N(4)-C(7)-C(12)-C(11) which are 179.41(17)°, -177.44(16)°, -178.18(15)°, 179.09(16)°, -178.7(2), -178.62(17)°, respectively. The corresponding data for the H-bonds are listed in Table. 5. The anionic picrate ion and the cationic 3-methyl anilinium ion in the charge transfer complex salt MTP form five intermolecular hydrogen bonds namely N(4)-H(4A)·····O(7), N(4)-H(4A)·····O(5), N(4)-H(4B)·····O(7), N(4)-H(4B)·····O(1) and N(4)-H(4C)·····O(4) with a donor-acceptor distance of 2.749(2), 2.970(2), 2.758(2), 2.977(16) and 2.887(2) respectively. The packing diagram (Fig. 6) indicates the existence of intermolecular hydrogen bonds in the three dimensional network between the constituent ionic species.

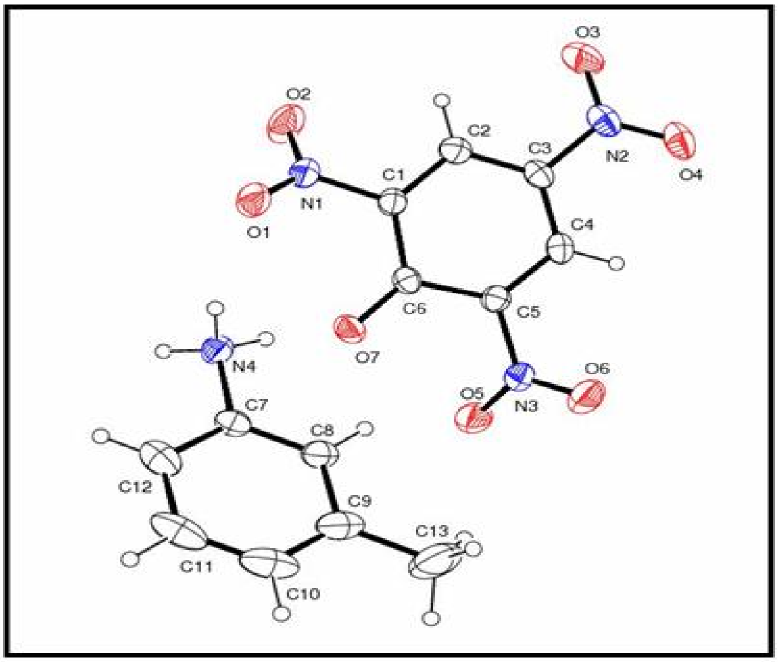


Fig. 5. ORTEP plot of MTP

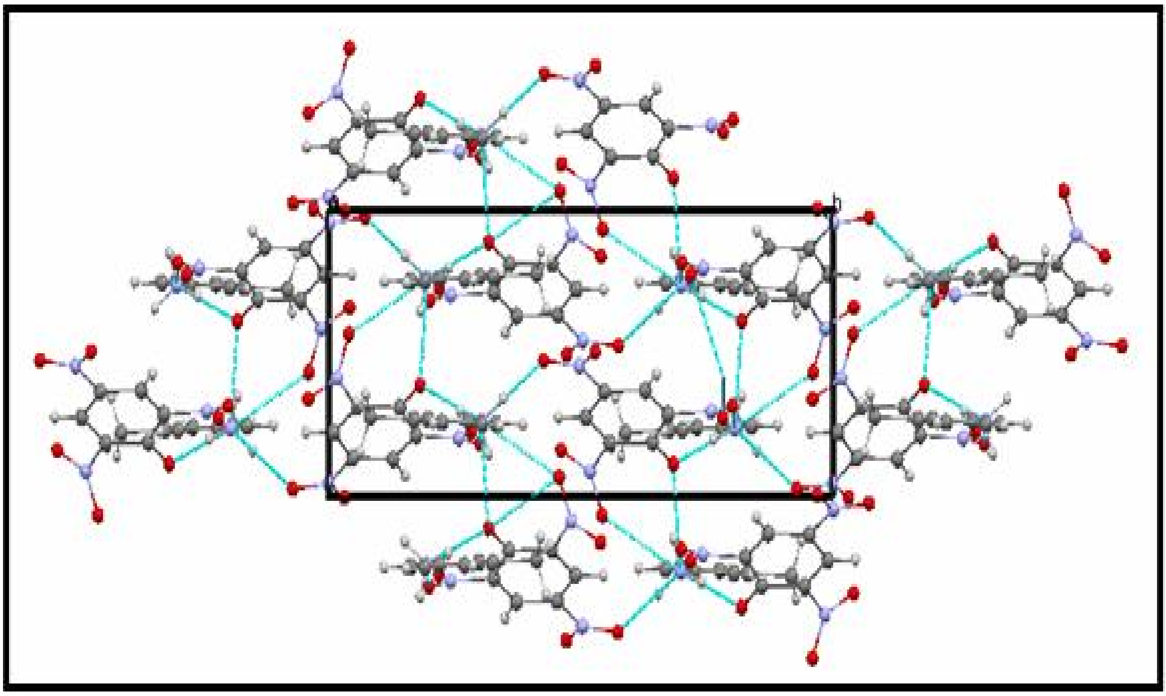


Fig. 6. Packing arrangement of molecules viewed down in the c-axis, showing intermolecular N-H···O hydrogen bonding.

3.4. UV-Vis-NIR transmittance studies

The recorded optical transmittance spectrum of MTP is shown in Fig. 7. The lower cut-off wavelength of the MTP crystal was around 488 nm. The attained percentage of transmittance was around 98 % in the wavelength range between 510 and 1100 nm. This crystal can be used for the suitable optical applications due to its wide transparency window in the part of visible region above 488 nm and in the near infrared region.

3.5. Fluorescence emission studies

Fluorescence may be normally expected in molecules that are aromatic or contain multiple conjugated system double bonds with a high degree of resonance stability[25]. The fluorescence emission spectrum was recorded in the range 500 to 900 nm and depicted in Fig. 8. A peak at 564 nm was observed in the emission spectrum. The results indicate that MTP crystal has a green fluorescence emission.

3.6. TG/DTA analyses

The thermal stability of the title salt crystal was established by TG and DTA analyses and the sample was analyzed between the temperatures 26 and 500°C at a heating rate of 10 K/min in nitrogen atmosphere and the thermogram is depicted in Fig. 9. The DTA reveals exactly same changes shown by the TGA. From the thermo gravimetric curve it is inferred that the material decomposes immediately after melting into gaseous products like H_2, NO_2, NO, methyl radical, hydrocarbon gases etc and the decomposition processes take place in two stages. The material exhibits sharp weight loss starting at 160°C and below this temperature no significant weight loss is observed. Hence the compound is stable upto 160°C. The first stage weight loss was observed between 160 and 218°C with the elimination of 27.03 % material illustrates the sublimation of the material followed by decomposition. The second stage weight loss noticed between the temperature 218 and 497.9°C incurs a weight loss of 49.89 % of the material into gaseous products.

From the DTA trace, it is observed that there is an endothermic peak starting at 184.4°C, which corresponds to the melting point of the compound. This is followed by a broad endotherm at 261.0°C and another endothermic peak at 389.4°C, which may be attributed to the second and third decomposition temperatures of MTP crystal respectively.

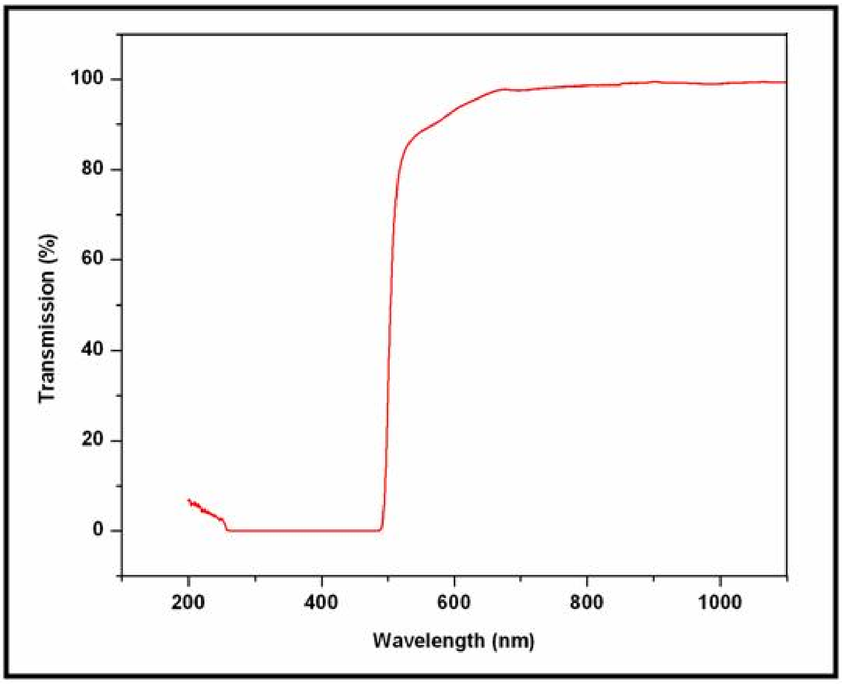


Fig. 7. Optical transmission spectrum of MTP

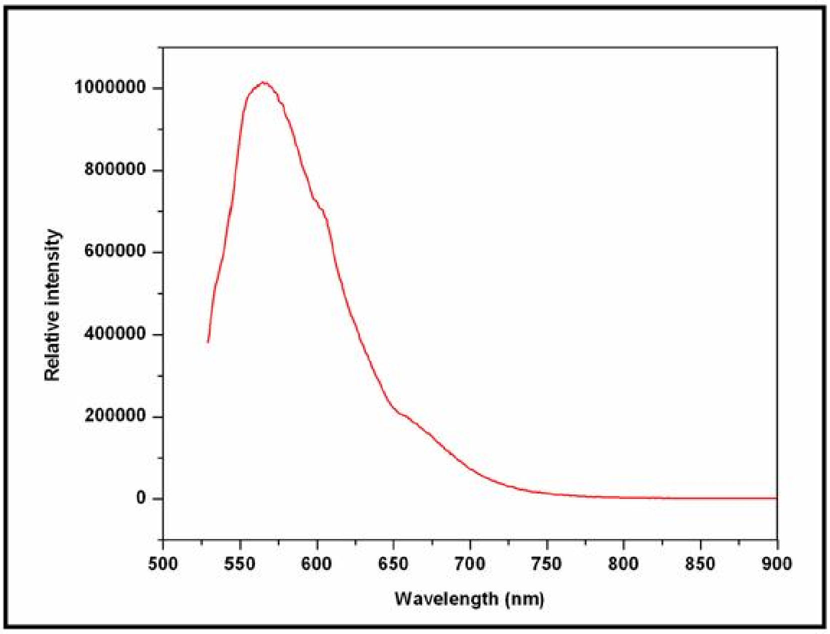


Fig. 8. Fluorescence emission spectrum of MTP

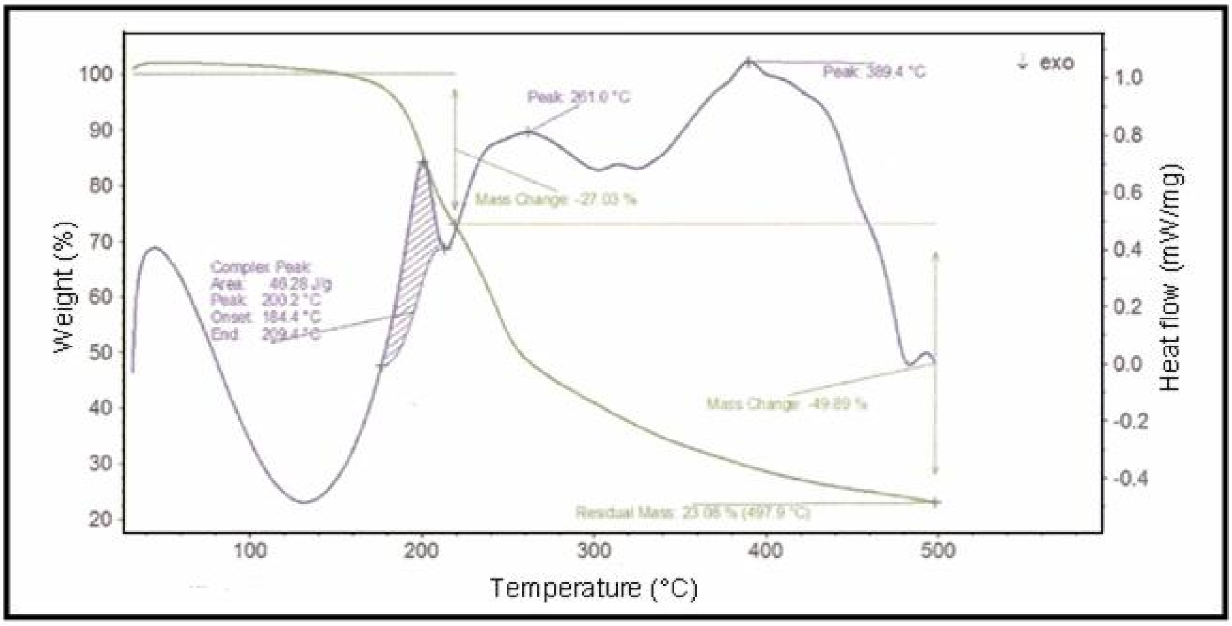


Fig. 9. TG/DTA thermogram of MTP

4. Conclusion

The organic charge transfer molecular complex salt of m-Toluidinium picrate was synthesized and the single crystals were grown by slow solvent evaporation solution growth technique in ethanol as solvent at ambient temperature. FT IR and NMR spectroscopic studies confirm the formation of the (1:1) adduct of MTP. The single crystal X-ray diffraction study revealed that MTP crystallizes in monoclinic crystal system with $P2_1/c$ space group. The UV-Vis-NIR spectrum of MTP in DMSO solution exhibits a wide transparency in the region between 488 and 1100 nm. The fluorescence emission analysis confirms a green emission from the MTP crystal. The thermal behavior of the title crystal was investigated by TG/DTA thermal analyses.

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