Synthesis, growth, spectral, and thermal studies of a new organic molecular charge transfer complex crystal: 3-Nitroaniline 4-methyl benzene sulfonate

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HIGHLIGHTS

- The structure reported for the first time in literature.
- The single crystals were grown from solution growth technique at room temperature.
- The charge transfer complex thermally stable upto 215 °C.
- Synthesis, structure and spectroscopic characterization were discussed.

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ABSTRACT

A new organic intermolecular charge transfer complex 3-nitroaniline 4-methyl benzene sulfonate (NATS) has been successfully synthesized and good optical quality single crystals grown by slow solvent evaporation solution growth technique at room temperature using methanol as the solvent. The \textsuperscript{1}H and \textsuperscript{13}C NMR spectra were recorded to establish the molecular structure of the title complex. The crystal structure of NATS has been determined by single crystal XRD analysis and it belongs to orthorhombic crystal system with space group Pbc\textsubscript{a}. Fourier transform infrared (FT-IR) spectral study has been carried out to confirm the presence of various functional groups present in the complex. Electronic absorption spectrum was recorded to find the prevalent charge transfer activity in the complex. The UV–Vis–NIR transmission spectrum was recorded in the range 200–2500 nm, to find the optical transmittance window and lower cut off wavelength of the title crystal. The thermal stability of the title complex crystal was studied by using thermo-gravimetric and differential thermal analyses and found that the compound is stable up to 215 °C.

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Introduction

Organic intermolecular charge transfer complexes have received a great deal of attention due to their wide range of applications in various fields like optical, magnetic, electrical and biological fields [1–9]. Due to their high electrical conductivity associated with the close molecular packing makes organic charge transfer complexes good semi and superconducting materials and found applications in solar cells [10–12]. Many mono- and poly nitro compounds form loose \pi-molecular complexes with various aromatic hydrocarbons, phenols, amines, etc. These complexes are called charge transfer complexes. Such complexes usually contain the components in the equimolar ratio and are generally

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colored [13–16]. They contain a donor and acceptor molecules in which an electron is partially transferred from the former to the latter. The donor molecule is an electron rich aromatic compound, an olefin or a molecule with unshared pair of electrons. The acceptor may be a proton, a Lewis acid, a halogen, an electron poor aromatic ring or a transition metal ion. Organic molecules with electron releasing substituent act as an electron donor and organic molecule with electron withdrawing substituent act as an acceptor. Charge transfer complexes are held together by weak intermolecular forces like van der walls force and hydrogen bonding. These complexes are characterized by the appearance of a new absorption band in the UV or Visible part of the spectrum at a longer wavelength than any of the component spectra and are known as charge transfer band. This band arises due to the transition of an electron from the highest occupied molecular orbital of the donor (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the acceptor. Hydrogen bonding is a versatile intermolecular force which is responsible for the close packing of molecules and enhances the thermal and mechanical stability of the crystal [17,18]. The charge transfer interaction accompanied with the intermolecular hydrogen bonding enhances the second order hyperpolarizability-β, and thereby increase the second harmonic generation of the crystal [19,20]. This paper presents the results obtained from the electronic and vibrational absorptions and nuclear magnetic resonance spectroscopic studies on the charge transfer complex formed between p-toluene sulfonic acid as an electron donor and the m-nitroaniline as the electron acceptor. The molecular structure, charge transfer interaction and thermal stability of the title complex have been established with the help of NMR, single crystal XRD, FT-IR spectra, electronic absorption spectral and TG/DTA thermal analyses.

**Experimental procedure**

**Material synthesis**

The title complex (NATS) was synthesized from 3-nitroaniline and p-toluene sulfonic acid taken in the equimolar ratio. The calculated amounts of reactants were dissolved separately in methanol and thoroughly mixed together. The resulting solution was stirred well for about an hour, when a yellow colored crystalline precipitate of the complex viz., 3-nitroaniline 4-methyl benzene sulfonate was obtained. The product was filtered off, dried and repeatedly recrystallized from methanol to enhance the purity of the material. Fig. 1 represents the reaction scheme involved.

**Crystal growth**

The saturated solution of the title complex was prepared using distilled methanol, and then the solution was heated gently to ensure the complete dissolution of the title complex. The solution was filtered to remove the suspended impurities. The clear filtrate so obtained was kept in an environment conducive for the growth of single crystals. Yellow colored transparent good optical quality single crystals of NATS were obtained within a period of ten days. The photograph of the as-grown crystals are shown in Fig. S1.

![Fig. 1. Reaction scheme of NATS.](image_url)

**Characterization**

To confirm the molecular structure of NATS crystal, the 1H and 13C NMR spectra were recorded employing a Bruker 500 MHz spectrometer in deuterated methanol as solvent using TMS as the internal reference standard. The crystal structure was determined from the single crystal X-ray diffraction data obtained with an Bruker Kappa Apex-II diffractometer (Graphite monochromated, Mo Kα = 0.713). The data were collected at 25 °C and the crystal data and structure refinement are given in Table 1. The structure was solved by direct methods using the program SHELXS-97 [21] and refined by full matrix least squares method using the program SHELXL-97 [22]. The R-value of the full-matrix least squared refinement is given in Table 1. The H-atoms could all be located in Fourier difference maps. FT-IR spectrum was recorded using potassium bromide pellet method employing a Perkin Elmer FT-IR spectrometer in the range 4000–450 cm⁻¹. The UV–Vis absorption spectrum of NAT was recorded employing a SYSTRONICS make double beam UV–Vis spectrometer 2202. The TGA and DTA studies were carried out on a SII Nanotechnology TG/DTA 6200 instrument at a heating rate of 10 °C/min in the temperature range from 20 to 800 °C in nitrogen atmosphere.

**Results and discussion**

**NMR spectral studies**

The 1H NMR spectrum of NATS complex is depicted in Fig. S2. In the 1H NMR Spectrum the appearance of six distinct proton signals confirms six different proton environments and thus the molecular structure of the NATS complex. The intense proton signal at δ 2.377 ppm is attributed to the methyl protons of 4-methyl benzene sulfonate moiety. The doublet proton signal centered at δ 7.230 ppm is attributed to the C3 and C5 protons of the same kind in 4-methyl benzene sulfonate moiety. The doublet proton signal appearing at δ 7.690 ppm owes to the C2 and C6 protons of the same kind in 4-methyl benzene sulfonate moiety. The doublet proton signal centered at δ 7.785 ppm is due to the C4 and C6 protons of the same kind in 3-nitroanilinium moiety. The triplet proton signal at 8.247 ppm is due to the C5 proton of 3-nitroaniline.
moiety. The singlet proton signal appearing at 8.30 ppm owes to the C2 proton of 3-nitroanilinium moiety. The N–H proton of 3-nitroaniline moiety in the complex are far downfield shifted and do not appear in the spectrum.

The $^{13}$C NMR spectrum of NATS complex is depicted in Fig. S3. The appearance of eleven distinct carbon signals in the spectrum unambiguously confirms the molecular structure of NATS. The carbon signal appearing in the upfield at $\delta$ 19.90 ppm is attributed to the methyl carbon of 4-methyl benzene sulfonate moiety. The carbon signal at $\delta$ 148 ppm owes to the C3 carbon of 3-nitroaniline moiety. The remaining carbon signals and their respective assignments are given in Table S1. Thus the molecular structure of NATS complex crystal explicitly gets confirmed from the $^1$H and $^{13}$C NMR spectral data.

**Single crystal X-ray diffraction studies**

Single crystal suitable for X-ray crystallographic analysis was selected following the examination under a polarizing microscope. X-ray intensity data of 11,877 reflections (of which 3547 were unique) were collected on a Bruker Kappa Apex-II diffractometer equipped with graphite monochromated Mo Kα radiation ($\lambda = 0.71073 \text{ Å}$). The cell dimensions were determined by least-squares fit of angular settings of 11,877 reflections in the $\theta$ range from 2.97° to 28.32°. The intensities were measured by $\omega$ scan mode for $2\theta$ ranges from 2.97° to 28.32°. The data were collected for Lorentz polarization and absorption factors. The structure was solved by direct methods using SHELXS97. All non hydrogen atoms of the molecule were located in the best E-map. Full-matrix least squares refinement was carried out using SHELXL97 and the final refinement cycles converged to an $R$ value of 0.0508 and $wR(F^2) = 0.1344$ for the observed data. Residual electron densities ranged from 0.586 to $-0.308 \text{ Å}^3$. Geometry of the molecule was found out using the WinGX [23] and PARST [24] software’s. The crystal data and details pertaining to data collection and the structure refinement are given in Table 1. Fig. 2 shows the ORTEP view of the molecule drawn at 40% probability thermal displacement ellipsoids with the atom numbering scheme. The packing arrangement of molecule viewed down the $a$-axis is shown in Fig. S4. The hydrogen bonding parameters were given in Table 2.

**FT-IR spectral analysis**

The FT-IR spectrum of NATS complex is depicted in Fig. 3. The formation of the intermolecular charge transfer complex is strongly evidenced by the presence of the characteristic infrared bands of the donor and acceptor molecules in the spectrum. From the spectrum it is observed that the bands of the donor are slightly shifted to lower frequency and that of the acceptor are slightly shifted to higher frequency. This shift in frequency is attributed to the changes in the electronic concentration upon the formation of charge transfer complex. The band observed at 3444 cm$^{-1}$ is due to the associated N–H stretching vibrations of 3-nitroaniline moiety. The absorption bands at 3088 and 3049 cm$^{-1}$ correspond to the asymmetric and symmetric aromatic C–H stretching vibrations respectively. The C–H asymmetric and corresponding

<table>
<thead>
<tr>
<th>D---H</th>
<th>A</th>
<th>D---H (Å)</th>
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<th>A (Å)</th>
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<th>&lt;D---H</th>
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<td>2N(2)---H(2A)---O(5)</td>
<td>0.75</td>
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<tr>
<td>2N(2)---H(2B)---O(5)</td>
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<td>2.56(3)</td>
<td>2.889(3)</td>
<td>103(2)</td>
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</tr>
<tr>
<td>2N(2)---H(2B)---O(4)</td>
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<td>1.98(3)</td>
<td>2.784(3)</td>
<td>154(3)</td>
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<tr>
<td>2C(3)---H(3)---O(5)</td>
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<td>2.59</td>
<td>3.297(3)</td>
<td>133</td>
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<tr>
<td>1C(8)---H(8)---O(3)</td>
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<td>2.55</td>
<td>3.912(3)</td>
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<tr>
<td>1C(9)---H(9)---O(1)</td>
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<td>3.482(3)</td>
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</table>

**Fig. 2.** ORTEP view of NATS crystal.

**Fig. 3.** FT-IR spectrum of NATS crystal.

**Fig. 4.** Electronic absorption spectrum of NATS.
symmetric stretching vibrations of the methyl group are observed at 2918 and 2858 cm\(^{-1}\) respectively. The characteristic NO\(_2\) asymmetric and symmetric stretching vibrations are observed at 1531 and 1350 cm\(^{-1}\) respectively. The aromatic C\(\equiv\)C stretching vibrations are exhibited at 1608, 1585 and 1398 cm\(^{-1}\). The C\(\equiv\)H in-plane bending vibration and the C\(\equiv\)H out of plane bending vibrations are observed at 1217 cm\(^{-1}\) and 732 cm\(^{-1}\) respectively. The asymmetric SO\(_3\) stretching vibration brings forth a strong band at 1120 cm\(^{-1}\) and the corresponding symmetric vibration shows a band of medium intensity at 1035 cm\(^{-1}\). The C\(\equiv\)N stretching vibration appears at 848 cm\(^{-1}\). The NO\(_2\) bending vibration is observed at 678 cm\(^{-1}\). The vibrational bands observed below 500 cm\(^{-1}\) are due to the skeletal vibrations.

UV–Vis spectral analysis

The recorded UV–Vis absorption spectrum of NATS complex is shown in Fig. 4. The spectrum exhibits the characteristic absorption band attributed to the charge transfer interaction in addition to the usual \(\pi-\pi^*\) and \(n-\pi^*\) bands of 3-nitroaniline and 4-methyl benzene sulfonate moieties of the title complex. This charge transfer band arises due to the promotion of an electron from donor 4-methyl benzene sulfonate molecule to the acceptor 3-nitroaniline molecule and appears on the longer wavelength of the spectrum at 371 nm. This band confirms the presence of intermolecular charge transfer activity in the title complex. The band due to \(\pi-\pi^*\) transition almost overlaps with the band due to CT transition. The \(n-\pi^*\) transition expected to occur on the longer wavelength region is getting submerged under the more intense \(\pi-\pi^*\) band.

UV–Vis–NIR spectral analysis

The recorded UV–Vis–NIR transmission spectrum of NATS crystal is shown in Fig. 5. The attained percentage of transmittance was 80% in the visible region. As has been observed in the spectrum there is no significant absorption in the entire visible region and near infrared region. The lower wavelength cut-off is around 300 nm. The crystal has a wide transparency window in the entire visible and NIR regions up to 2500 nm enabling the title crystal a potential candidate for the optical applications.
TG/DTA thermal analyses

The thermal stability of NATS crystal has been established by simultaneously employing thermo gravimetric and differential thermal analysis and the thermogram is depicted in Fig. 6. The DTA thermogram reveals the same changes shown by TGA thermogram. From the TG curve it is understood that the title complex is stable up to 215 °C and it decomposes immediately after melting. The decomposition occurs in a single stage. TG thermogram further indicates that the complex material decomposes into various gaseous products like SO2, NO2, NH3, etc. which account for the total weight loss of 68%. This is further confirmed by DTA. The sharp endothermic dip at 215 °C corresponds to the melting point of the complex. The exothermic peak around 288 °C indicates that the major decomposition temperature of the substance.

Conclusions

The new organic intermolecular charge transfer complex 3-nitroaniline 4-methyl benzene sulfonate was synthesized and single crystals were grown by the slow solvent evaporation solution growth technique at ambient temperature. The crystal structure was established by single crystal XRD analysis. The title crystal belongs to orthorhombic crystal system with Pbc a space group. The presence of various functional groups in the title complex has been confirmed by FT-IR spectroscopic study. The 1H and 13C NMR spectroscopic study confirms the established molecular structure of the complex crystal. The UV–Vis absorption spectrum substantiates the prevalent charge transfer activity in the title complex. The UV–Vis–NIR transmission spectrum suggests the suitability of NATS crystal for various optical applications. The thermal stability of the title crystal was determined by TG/DTA studies.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2013.11.029.

References