SUMMARY

Studies on organic picrate complexes were undertaken in order to find out their potential use in various fields. In the present work systematic studies were undertaken on the picrate complexes synthesized. The following six picrate complexes were synthesized by slow evaporation solution growth method at room temperature.

1. Benzotriazolinium picrate \( \text{BTP} \)
2. 4-Hydroxytetrarmethylpiperazinium picrate \( \text{TMPP} \)
3. 4-Piperidinium carboxylamide picrate \( \text{PCP} \)
4. 3,5 Dimethylpyrazolium picrate \( \text{DMPP} \)
5. 4-Dimethylaminopyridinium picrate \( \text{DAPP} \)
6. 2-Methylimidazolium picrate \( \text{MIMP} \)

The above six picrate complexes were repeatedly recrystallized to get good quality of crystals. The synthesized complexes were characterized by elemental analysis, solubility study, powder X-ray diffraction method, UV-visible absorption, UV-visible transmittance, band gap energy, emission spectrum and thermogravimetry, differential thermal analysis, differential scanning calorimetry, single crystal X-ray diffraction and fourier transform infrared, polarized Raman and nuclear magnetic resonance spectra. The microhardness measurement, dielectric, nonlinear optical property and antimicrobial activity studies were also carried out. The following conclusions are obtained.

- The stoichiometric ratios of the complexes were confirmed by elemental analysis.
- The solubilities of the complexes in methanol and acetone were studied at different temperatures and observed that all the complexes were more soluble in methanol than in acetone. Methanol was used solvent for growing the crystals.
- The UV-visible absorption spectral analysis indicates that the complexes, BTP, PCP and MIMP show \( \pi-\pi^* \) transitions and the complexes, TMPP, DMPP and DAPP show \( n-\pi^* \) and \( \pi-\pi^* \) transitions
• The cut-off wavelengths and transparencies of the complexes measured by UV-visible transmittance spectral study show the cut-off wavelengths in the region from 360 to 380 nm which are due to the $\pi-\pi^*$ transition in the complexes.

• The powder X-ray diffraction of the complexes indicated the crystalline nature of the complexes. The predominant peaks in the powder X-ray diffraction pattern were indexed. The unit cell parameters obtained from the powder X-ray diffraction pattern of all the complexes fit with the unit cell parameters obtained from the single crystal X-ray diffraction pattern.

• The band gap energies of the complexes were calculated from the transmittance data. The band gap energies of the complexes, BTP, TMPP, PCP, DMPP, DAPP and MIMP were found to be 1.76, 2.00, 1.79, 1.80, 2.10 and 1.79 eV respectively.

• The decomposition patterns and thermal stabilities of the complexes were studied by TG-DTA analyses. The thermal studies indicate that the complexes, TMPP, DMPP and MIMP were stable up to 140°C, 140°C and 233°C respectively. The DTA studies of the complexes were in good agreement with the TG studies.

• The emission spectral study indicates that the complexes, BTP, PCP and MIMP show green fluorescence emission and the complexes, TMPP, DMPP and DAPP show green and red fluorescence emissions.

• The low temperature DSC analyses of the complexes show thermal anomalies in the heating and cooling cycles. The complexes show first order phase transitions which may be due to the some structural changes in the complexes.

• The complexes were characterized by FTIR and polarized Raman spectral analyses.

• The different kinds of protons and carbons in the complexes were ascertained by $^1$H and $^{13}$C NMR spectroscopic techniques.

• The SHG efficiencies of the complexes were studied by Kurtz-Perry powder technique. These results indicate that the complexes, BTP, TMPP, PCP, DAPP and MIMP have SHG efficiency 2, 1.5, 5, 32 and 2 times greater than that of the standard KDP respectively. The SHG efficiency of DMPP complex was confirmed by emission of green light. The SHG efficiencies of the complexes are due to the presence of impurities, zero field defects and also the packing of hydrogen bonds in the crystal lattice.
• The mechanical properties of the complexes were measured by Vicker’s microhardness test and found that the complexes, BTP, TNMPP, PCP, DMPP were soft materials and the complexes, DAPP and MIMP were hard materials.

• The dielectric constant and dielectric loss of the complexes were studied in the frequency region from 50 Hz to 5 MHz. The dielectric constant and dielectric loss of the complexes decreased with increase in frequency. The value of dielectric constant and dielectric loss were high at lower frequency region and low at higher frequencies. The low values of dielectric loss for the complexes indicate that the synthesized complexes can be useful for optoelectronic applications.

• The in vitro antibacterial and antifungal activities of the complexes were studied by disc diffusion method. The results of the complexes show that all the complexes exhibit significant inhibition activities against various bacteria and fungi species.

• The structures of the complexes were determined by single crystal X-ray diffraction analyses. It was found that the complexes, BTP, TMPP, PCP and DMPP crystallized in monoclinic systems with P2(1)C space groups whereas the complexes DAPP and MIMP crystallized in monoclinic system, P2(1)/n and monoclinic system, C2/C space groups respectively. In all the complexes the mono pronated cation and deprotonated anion were present in the crystal lattice. The hydrogen bonded network of the complexes clearly show that in all the complexes the cation parts are joined to the anionic parts through extensive hydrogen bonding. The cations and anions in the complexes were linked by strong N-H…O, N-H…N and C-H…O hydrogen bonds. These hydrogen bonds are responsible for the stability of the complexes. The combination of hydrogen bonds forms three dimensional networks.