



REVIEW ARTICLE

REVIEW ON SYNTHESIS, SPECTRAL, ANTIMICROBIAL PROPERTIES OF AN ORGANIC CHARGE TRANSFER PICRATE COMPLEXES

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Abstract

A survey of literature indicates that an extensive work has been done on various picrate complexes. Realising the importance of the complexes, we undertook the synthesis and characterization of some of the organic picrate crystals. The complexes were characterized by spectral, structural, thermal, optical, dielectric, mechanical and antimicrobial studies. The following six organic picrate complexes were synthesized and characterized. The synthesized complexes were grown by slow evaporation solution growth method at room temperature and were characterized by elemental analysis, solubility study, powder X-ray diffraction, single crystal X-ray structure analysis and UV-visible, emission, Fourier transform infrared (FTIR), polarized Raman and nuclear magnetic resonance (NMR) spectra. Thermogravimetric analysis (TGA), differential thermal analysis (DTA), differential scanning calorimetry (DSC) and microhardness measurement, dielectric, nonlinear optical property (NLO) and antimicrobial activity studies were also carried out.

Keywords: Picrate complexes, Spectral, Structural, Optical, Dielectric, Antimicrobial studies.

Introduction

Picric acid has a tendency to form stable picrate compounds with various organic molecules due to the presence of active electron cloud and ionic bonds (Yamaguchi et al., 1988). In the past two decades, organic nonlinear optical (NLO) picrate crystals have attracted the scientists and technologists due to their potential applications in the area of photonics including optical information processing (Prasad, 1991; Marder et al., 1991; Saleh, M.C. Teich, 1991; Penn et al., 1991), high-energy lasers for inertial confinement fusion research, colour display, electro-optic switches, frequency conversion, etc. (Badan, et al., 1993). The organic picrate compounds exhibit larger NLO response

than inorganic materials due to the presence of active π -bonds. However, these materials have poor mechanical strength, thermal stability, laser damage threshold, etc., than the inorganic materials. As the organic materials possess prominent NLO properties, new organic NLO materials are synthesized and characterized. A detailed survey of literature on picrate crystals are presented in this chapter.

Paula Zaderenko *et al.* (1997) studied the crystal structure of the diethyl 2-benzimidazol-1-ylsuccinate-picrate. The structure of the crystal was determined by single crystal X-ray diffraction analysis. The X-ray diffraction analysis indicated that the compound belonged to orthorhombic crystal



system with $Pna2_1$ space group. Cross Polarization and Magic Angle Spinning (CP/MAS) and solid NMR studies showed that the picric acid linkage depends on the nature of the azole group.

Neodymium and europium 3-picoline-N-oxide picrate complexes were synthesized by Freitas Nunes *et al.* (1999). Single crystal X-ray diffraction method indicated that the synthesized Eu complex crystallized in triclinic system with space group $P\bar{1}$. The emission spectrum of the complex showed the existence of two different Eu(III) coordination environments.

The crystal structure, IR absorption spectra, emission spectrum of the europium compound, TG and DSC analyses of lanthanide 4-methylmorpholine N-oxide picrate complexes were reported by Fernandes *et al.* (2000). The grown crystals crystallized in triclinic crystal systems with $P\bar{1}$ space groups as determined by single crystal X-ray analysis. Thermal analysis showed that the Eu(III) crystal was thermally stable up to 300°C.

Szumna *et al.* (2000) synthesized the 1,5-diamino-3-oxapentane, 1,8-diamino-3,6-dioxaoctane and 1,5-diamino-3-azapentane picrate complexes. The crystal structures of the crystals were characterized by single crystal X-analysis. The synthesized crystals crystallized in monoclinic systems with $P2_1/c$ space groups. The FTIR and UV spectral characterizations were also carried out.

Terbium(III), holmium(III) and erbium(III) picrate complexes were characterized by Cardoso *et al.* (2002). The single crystal X-ray diffraction study revealed that the Tb compound belonged to triclinic crystal system with $P\bar{1}$ space group. TG analyses indicated that the water molecules eliminated followed by decomposition of picrates.

The 1:1 and 2:1 picrate complexes of N-methylmorpholine betaine were prepared

and their structures determined by single crystal X-ray diffraction method by Dega-Szafran *et al.* (2002). The single crystal X-ray diffraction study indicated that the crystal systems of the 1:1 and 2:1 complexes were orthorhombic, $Pbca$ space group and monoclinic, $P2_1/c$ space group respectively. The FTIR and NMR spectra were also discussed.

Hydrated Sc(III) picrate compound was prepared by Sanchez *et al.* (2002). The compound crystallized in monoclinic system with $C2/c$ space group. The luminescence, phosphorescence and excitation spectra were also carried out.

Carvalho *et al.* (2003) have reported the unit cell parameters of the 8-Hydroxyquinolinium picrate. The unit cell parameters indicated that the complex crystallized in monoclinic with $P2_1/c$ space group. The symmetry and the number of internal modes were observed in the polarized Raman and infrared spectra.

Hydrated Lanthanide(III) nicotinamide N-oxide picrate complexes were prepared by Bombieri *et al.* (2003). The structures of Pr, Nd and Tm complexes were established by X-ray crystallography method. The prepared Nd and Tm complexes crystallized in triclinic systems with $P\bar{1}$ space groups. The complexes were also characterized by elemental analysis and IR spectrum.

Giovanni Tazher *et al.* (2003) studied Ni(II) pseudo-octahedral picrate complexes. The synthesized complexes were analyzed by elemental, FTIR and single crystal X-ray diffraction analyses. The single crystal X-ray analysis indicated that the crystal systems of the compounds were monoclinic with $P2_1/n$ space groups.

The single crystal structures of 2,6-di-*t*-butyl-picrate (dbpH) and metal substituted 2,6-di-*t*-butyl-picrate derivatives were reported by Lynch *et al.* (2003). The SHG study results indicated that the dbpH was

non-centrosymmetric and an ungraded powder sample exhibited SHG optical intensity five times greater than that of ungraded urea sample. The single crystal X-ray diffraction method showed that the compounds belonged to monoclinic systems with $P2_1/c$ space groups.

The crystalline salt of prolinium picrate was studied by Zhi Min Jin *et al.* (2003) and characterized by FTIR and X-ray crystallography analyses. The single crystal X-ray diffraction method revealed that the crystal system of prolinium picrate was orthorhombic with P_{212121} space group.

El-Medani *et al.* (2003) synthesized the 1:1 picrate (PA) complexes of 2-aminobenzimidazole (ABZ) and trinitrobenzene (TNB). The crystal structures of the complexes were determined by single crystal X-ray diffraction method. The ABZ-PA complex crystallized in triclinic system with $P2_1$ space group, while the TNB-PA adduct crystallized in monoclinic system with $P2_1/c$ space group.

Solid complexes of lanthanide picrates were prepared by Ya-Wen Wanga *et al.* (2003). The grown crystals were characterized through elemental, FTIR, 1H NMR and single crystal X-ray diffraction techniques. The single crystal X-ray analysis indicated that the synthesized crystal belonged to monoclinic system with $P2_1/c$ space group. It is almost a well proven fact by both theory and experiment that to possess good second harmonic generation efficiency, the material should have a non-centrosymmetric crystalline structure. However, there are some reports available in the literature establishing the fact that the centrosymmetric crystals or films can also exhibit NLO properties. A centrosymmetric crystal can be made into a SHG active material with lesser number of defects (Suresh *et al.*, 2012). An organic molecule should have high second order hyperpolarizability ($\chi^{(2)}$) to exhibits large NLO

properties. The hyperpolarizability can be enhanced by increasing intermolecular charge transfer interaction by extending π -conjugated system (Benet and B. Sahraoui, 2004; De Matos Gomes *et al.*, 2000). Most of the complexes of picric acid encourage acentric packing which results in large hyperpolarizability ($\chi^{(2)}$) and remarkable second order NLO activity ($\chi^{(2)}$) (Kityk *et al.*, 2004).

Dega-Szafran *et al.* (2004) have reported the picrate complexes of 1-piperidiniumacetate and 1-piperidiniumacetic acid. The complexes crystallized in monoclinic systems with $P2_1/c$ space groups and $Z = 4$. The presence of protonated 1-piperidineacetic acid and its zwitterion in the crystal were confirmed by ^{13}C CP/MAS NMR and solid state FTIR spectral analyses.

Anitha *et al.* (2005) have reported crystal structure of L-Asparazinium picrate. The single crystal X-ray analysis indicated that the compound belonged to monoclinic system with $P2_1/c$ space group. The supramolecular chemistry and crystal structures of two concomitant polymorphs of betaine and imidazole picrate complexes were studied by MacDonald *et al.* (2005). The single crystal X-ray diffraction data showed that the crystal systems of the betaine and imidazolium picrates were triclinic, $P\bar{1}$ space group and monoclinic, $C2/c$ space group respectively.

Pragati Agnihotri *et al.* (2005) have studied the dibenzo-30-crown-10 potassium picrate crystal. The synthesized crystal crystallized in monoclinic system with $C2/c$ space group. The UV-visible and NMR spectra were also studied to confirm the molecular structure of the crystal. Solid complexes of Pr and Nd picrates with a new amide type tripodal ligand, 2,2',2'' nitrilotris-(N-phenylmethyl)-acetamide were prepared by Yu Tang *et al.* (2005). The single crystal X-ray diffraction analysis indicated that the Pr and Nd compounds crystallized in

monoclinic systems with $P2_1/n$ space groups. The luminescent property of the Eu (III) complex was also described.

Charge-transfer complexes of 2,2-bipyridine picrate and chloranilate were reported by Said Teleb *et al.* (2005). The elemental, NMR and photometric titration results indicated that the complex was formed in 1:1 molar ratio. The formation constants of the complexes were shown to be dependent on the structure of the electron acceptors used.

Chuan-Ming Jin *et al.* (2005) have investigated the energetic mono and bridged imidazolium, triazolium, tetrazolium picrates and the dipicrates. The structures of tetrazolium picrates were determined by single crystal X-ray diffraction analysis. The grown triazolium and tetrazolium picrates crystallized in orthorhombic system, Pbcn space group and monoclinic system, C2/c space group respectively. The thermal study indicated that the grown picrates were thermally stable up to 176°C.

Solid complexes of biphenyl, N-benzyl-2-{20-[(benzyl-methyl-carbamoyl)-methoxy]-biphenyl-2-yl-oxy}-N-methyl-aceamide lanthanide picrates were studied by Kuan-Zhen Tang *et al.* [44]. The crystal systems of the complexes were triclinic with $P1$ space groups. Briget Mary *et al.* (2006) have studied a comparative study of infrared and Raman spectra of dl-valine dl-valinium and dl-methionine dl-methioninium picrates at room temperature. The structures of these picrates were determined by single crystal X-ray diffraction method.

The FTIR and laser Raman spectra of -alanine -alaninium and dl-phenylalanine dl-phenylalaninium picrate crystals were reported by Briget Mary *et al.* (2006). The single crystal X-ray analysis indicated that the grown crystals were crystallized in triclinic systems with $P1(Ci)$ space groups. Fermi resonance was also

observed for one of the crystal -alanine -alaninium picrate.

Good quality single crystal of L-Asparaginium picrate was grown by Srinivasan *et al.* (2006). The relative SHG efficiency of the material was 66.5 times greater than that of KDP and 10 times greater than that of urea. The single crystal X-ray analysis revealed that the crystal system of the compound was monoclinic with $P2_1$ space group. The dielectric and mechanical behaviours of the specimen were also studied.

Density functional theory calculation of crystalline potassium picrate was performed by Xue-Hai *et al.* (2006). The grown crystal was characterized by band structure, lattice energy calculation and single crystal X-ray diffraction techniques. The X-ray diffraction study indicated that the compound belonged to monoclinic crystal system with $P2_1/c$ space group. The value of band gap energy for the crystal was 3.29 eV.

Sock-Sung Yun *et al.* (2006) have synthesized Ln(III) and Tb picrate complexes. The X-ray diffraction method showed that the crystal systems of the complexes were triclinic with $P1$ space groups. The TG-DTG and DSC thermal analyses revealed that the lanthanide complexes were thermally decomposed in three distinctive stages between 140°C and 560°C.

The tetraprotonated octaaminocryptand and triprotonated octaaminocryptand picrate complexes were studied by Ravikumar *et al.* [50]. The synthesized compounds were examined crystallographically and results indicated that the complexes crystallized in monoclinic system, C2/c space group and triclinic system, space group $P1$ respectively. Thermal analysis of the compounds was also carried out.

Krishnakumar *et al.* (2007) studied the nonlinear optical property of 8-hydroxyquinoline picrate. The crystal

belonged to monoclinic system with $P2_1/c$ space group. The good transparency was confirmed by optical transmittance studies. The FTIR, polarized Raman and third order nonlinear optical property were also studied. Solid complexes of lanthanide biphenyl derivative picrates were prepared by Yan-Ling Guo *et al.* (2007) and characterized by elemental, conductivity measurement, FTIR, single crystal X-ray diffraction and electronic spectroscopic studies. The single crystal X-ray analyses showed that the crystallized in triclinic crystal system with $P\bar{1}$ space group.

Chandramohan *et al.* (2007) have synthesized the single crystals of caffeine picrate. Single crystal X-ray analysis revealed that the crystal system of the material was monoclinic system with centrosymmetric $P2_1/n$ space group. The emission of green radiation by the complex confirmed that the material can be used as a NLO material. The thermal study indicated that the complex was thermally stable up to 142°C.

The synthesis of l-oxo-bis[nitrato dimethyl tellurium(IV)] (1), l-oxo-bis[(2,4,6-trinitro) phenolato dimethyl tellurium(IV)] (2) and l-oxo-bis[1-(2,4,6-trinitro) phenolato -1,1,2,3,4,5-hexahydro tellurophene] (3) picrates were reported by Srivastava *et al.* [54]. The X-ray diffraction method indicated that the compounds 1, 2 and 3 crystallized in monoclinic $C2/c$ space group, monoclinic $P2_1/c$ space group and tetragonal $P4C_2$ space group respectively. The UV-Vis, FT-IR, (1H , ^{13}C) NMR spectral analyses were also reported.

Senthilkumar *et al.* (2007) investigated the infrared and Raman spectra of L-valinium picrate at room temperature. The single crystal X-ray diffraction of the crystal data showed that the crystal system of the compound was monoclinic with $P2_1$ space group. The various functional groups were confirmed by spectral analyses. The selectivity factor and coordination behaviour of Lanthanum(III) picrates were studied by

Saleh *et al.* (2008). The structures of the complexes were studied by single crystal X-ray diffraction analysis. The La-Gd picrate complexes crystallized in orthorhombic systems with $Pbca$ space groups, while the Ho picrate complex crystallized in triclinic crystal system with $P\bar{1}$ space group.

A two-dimensional copper(II) picrate complex was synthesized by Zhi-Qiang Liu *et al.* (2008). The compound crystallized in monoclinic system with $P2_1/c$ space group as confirmed by single crystal X-ray diffraction analysis. The fluorescence titration revealed that the binding mode between the binuclear copper(II) complex and Herring Sperm DNA might be intercalation.

Charge transfer picrate complex, dimethyl-1, 10-phenanthroline picrate was studied by Gaballa *et al.* (2008). The elemental, IR and photometric titration studies indicated that the complex was formed in 1:1 molar ratio. The grown crystal crystallized in monoclinic system with $P2_1/n$ space group. Uma Devi *et al.* (2008) have grown L-prolinium picrate by temperature reduction method. The SHG efficiency of the crystal was 52 times greater than that of KDP. The single crystal X-ray diffraction technique showed that the grown crystal belonged to monoclinic crystal system with $P2_1/c$ space group.

First order hyperpolarizability of L-asparaginium picrate crystal was performed by Srinivasan *et al.* [60] using density functional theory calculations. The calculated first order hyperpolarizability of L-asparaginium picrate complex was 4.8152×10^{-29} esu. The crystalline material of acenaphthene picrate was grown by Chandramohan *et al.* (2008). The unit cell parameters of the compound was calculated and found that the compound belonged to monoclinic system with $C2/c$ space group. The material showed powder SHG efficiency was 0.39 times greater than that of urea.

Moamen Refat *et al.* (2008) have investigated N,N-bis-alkyl derivatives of 1,4,6,8-naphthalenediimide picrate complexes. The photometric titrations of the complexes showed that the complexes were formed in 1:1 molar ratio. The spectral and thermal characterizations were also studied. The single crystal of naphthalene picrate was synthesized by Chandramohan *et al.* [63]. Thermal behavior and stability of the crystal were studied using TG-DTA analyses and found that it was stable up to 151°C. The SHG nature of the compound was also studied.

Kirubavathi *et al.* (2008) have synthesized single crystal of L-valinium picrate by slow evaporation solution growth technique. The compound crystallized in monoclinic system with $P2_1$ space group. Optical properties of the crystal were confirmed by UV-visible study. The SHG efficiency of the crystal was twice than that of KDP.

Lakshminarayanan *et al.* (2008) have studied the multigram synthesis of an octaaminocryptand picrate complex. The material crystallized in monoclinic crystal system with $P2_1/c$ space group. The FT-NMR characterization was also carried out to confirm the molecular structure of the compound.

Ferrocene-based ammonium picrate compounds were reported by Petr Stepnicka *et al.* (2008). The SHG efficiency of the complex was measured and its efficiency compared with standard urea. The single crystal X-ray diffraction data revealed that the crystal systems of the compounds were triclinic with $P\bar{1}$ space groups. Thermal and spectral characterizations were also carried out.

Bharathikannan *et al.* (2008) have synthesized the organic NLO material, 2-nitroaniline picrate. The thermal stability of the crystal showed that the compound was thermally stable up to 81°C. The emission of

green radiation in SHG efficiency study confirmed that the compound can be used as an NLO material. The unit cell parameters of the crystal indicated that the compound crystallized in monoclinic system.

The donor-acceptor methamphetamine picrate complexes were studied by Parvin Shahdousti *et al.* (2008). The oscillator strengths, transition dipole moments and resonance energy of the complex in the ground state for all complexes were calculated. Vertical ionization potential of the donors and electron affinity of acceptors were determined by ab-initio calculation.

The N,N dimethyl anilinium picrate crystal was grown by Chandramohan *et al.* (2008). The SHG conversion efficiency of crystal was 1.29 times greater than that of urea. The unit cell parameters of the grown complex showed that the compound belonged to monoclinic system. FTIR and ^1H NMR spectral studies were also studied to ascertain the molecular structure of the complex.

Several substituted azolium picrate complexes were synthesized by Klapotke *et al.* (2008). The synthesized complexes were analyzed by using FTIR, NMR and single crystal X-ray diffraction analyses. The single crystal X-ray diffraction study revealed that the most of the azolium picrate complexes crystallized in monoclinic crystal systems with $P2_1/c$ space groups and the few complexes crystallized in triclinic systems with $P\bar{1}$ space groups.

L-Valinium picrate crystal was grown by Martin Britto Dhas *et al.* (2008) using slow evaporation method. The single crystal X-ray diffraction analysis showed that the crystal belonged to monoclinic crystal system with $P2_1/c$ space group. The SHG conversion efficiency of the compound was 60 times greater than that of the standard KDP and 8 times greater than that of the

standard urea. Microhardness and dielectric studies were also carried out.

Martin Britto Dhas *et al.* (2008) have also studied the L-prolinium picrate complex. The complex crystallized in monoclinic crystal system with $P2_1$ space group. The SHG efficiency of the complex was 74 times greater than that of the standard KDP. The dielectric study indicated that the sample possessed enhanced optical quality with lesser defects.

First order hyperpolarizability ($\chi^{(1)}$) value of L-valinium picrate single crystal was studied by Srinivasan *et al.* (2008). The SHG efficiency of the compound was high when compared to KDP. Planar molecular structure and charge transfer results indicated that the complex possessed larger values of $\chi^{(1)}$.

1:1 Glycine picrate crystal was synthesized by Uma Devi *et al.* (2008). The cell parameters of the complex showed that it crystallized in monoclinic system. Thermal analysis suggested that the crystal exhibited a single sharp weight loss at 214°C. The microhardness study indicated that the crystal was a soft material.

Petrosyan (2010) has synthesized the diglycine picrate crystal. The crystal system of the complex was monoclinic with $P2_1/c$ space group. According to his study the diglycine picrate was determined as 2:1 complex not as 1:1 complex.

The crystal structures of 2-amino-4,6-dimethoxypyrimidinium and 2,4-diamino-5-(4-chlorophenyl)-6-ethylpyrimidin-1-ium picrates were studied by Kaliyaperumal Thanigaimani *et al.* (2009). The single crystal X-ray study indicated that the grown crystals belonged to monoclinic crystal systems with $P2_1/c$ space groups. Qin Wang *et al.* (2009) reported the 20-[(1,2-naphthalene) bis (oxy)] bis[N (phenylmethyl)] acetamide substituted lanthanide picrate complexes. The grown

crystals crystallized in triclinic crystal systems with $P \bar{1}$ space groups as confirmed by single crystal X-ray analysis. The molar conductance and luminescence properties of the complexes were also carried out.

An organic nonlinear optical material, glycine picrate was studied by Uma Devi *et al.* [(2009). Etching study and the low values of dielectric constant with high frequency for the sample suggested that the material can be used in optical devices. The X-ray diffraction data showed that the crystal belonged to monoclinic system with $P2_1/a$ space group. The Z-scan measurements revealed that compound possessed prominent third order nonlinearity.

Good quality single crystal of picrate adduct, tri-*n*-nitrophenol methyl *p*-hydroxybenzoate was grown by Vesta *et al.* (2009). Single crystal X-ray diffraction analysis showed that the crystal system of the material was triclinic with $P \bar{1}$ space group. Thermal analysis indicated that the sample was stable up to 187°C. Optical absorption study revealed that the compound was well suited for optical applications.

Shakir *et al.* (2009) have studied the remarkable second-harmonic generation efficiency of glycine picrate crystals. The synthesized compound crystallized in centrosymmetric structure. The SHG efficiency of the crystal was 2.34 times greater than that of KDP. The absorption studies showed that the crystal was fully transparent to the green radiation to yield full SHG output. The dielectric and ac-conductivity characterizations were also studied.

Vesta *et al.* (2009) have studied the picrate adduct, tri-*n*-nitrophenol -*p*-hydroxyacetophenone. The synthesized crystal belonged to monoclinic system with $P2_1/c$ space group as determined by single crystal X-ray analysis. Thermal analysis

showed that the sample was thermally stable up to 135.1°C. The NLO study of the crystal showed that the complex had third order harmonic generation.

¹H NMR evidence for the pentaethylene glycol Ln(III) picrate complexes were studied by Eny Kusriani *et al.* (2009) The single crystal X-ray study showed that the both compounds were isostructural and crystallized in monoclinic systems with P2₁/c space groups. The molar conductance of the complexes indicated that both compounds were ionic in nature. The thermal properties were also studied using TG-DTA analyses.

Shakir *et al.* (2009) have synthesized bulk single crystals of glycine picrate by the slow cooling method. The crystal system of the material was monoclinic with P2₁/a space group. The SHG efficiency of the crystal was 2.34 times greater than that of KDP. The dielectric properties of the complex were also studied.

3,3-Dinitroazetidinium picrate complex was synthesized by Ma *et al.* (2010). The single crystal X-ray measurement analysis showed that the compound crystallized in orthorhombic system with P2₁2₁2₁ space group. The thermal behaviour of the complex was studied under a non-isothermal condition by DSC and TG-DTG methods. The free radical signals of the complex were detected by ESR technique to estimate its sensitivity.

Eny Kusriani *et al.* (2010) have studied the structure and magnetic properties of triethylene glycol praseodymium picrate complex. The complex belonged to triclinic crystal system with P 1 space group. The temperature dependence of the magnetic susceptibility of the complex showed the presence of weak antiferromagnetic interactions between the Pr(III) centres.

The charge transfer complexes of morpholine chlorate and picrate were investigated by Refat *et al.* (2010) . The

stability constant of the complexes were increased with high donation of morpholine. The IR, ¹H NMR and elemental analyses were also studied. The X-ray crystal structure analysis showed that the synthesized complexes crystallized in triclinic systems with P 1 space groups.

The charge transfer complex, *p*-toluidine picrate was studied by Neeti Singh *et al.* (2010). The spectroscopic and thermodynamic parameters showed that the complex was solvent dependent. The oscillator strengths, ionization potential, transition dipole moments, resonance energies and standard free energies results showed that the complex was stable, exothermic and spontaneous.

Anandhi *et al.* (2010) have reported the growth of single crystals of orthonitroaniline picrate. The single crystal X-ray diffraction data indicated that the crystal system of the compound was monoclinic. The Vicker's microhardness test showed that the complex belonged to soft material. Other characterizations were also carried out. Anandha Babu *et al.* (2010) reported the single crystal of dimethylammonium picrate. The thermal studies were used to study its thermal properties. The single crystal X-ray diffraction analysis revealed that the crystal crystallized in orthorhombic system with Pca2 space group. The SHG efficiency of the complex was twice than that of standard KDP.

The charge transfer complex, sulfamethoxazole picrate was studied by Refat *et al.* [90]. The TG-DTG analysis was used to investigate the thermal stability of the compound and found that the compound was stable up to 200°C. The stoichiometry of the complex was 1:1 molar ratio.

The formation of 1:1 hydrogen bonded charge transfer complex, *o*-phenylenediamine picrate was studied by Khan *et al.* (2010). The formation constant

and molar extinction co-efficient were evaluated by Benesi-Hildebrand equation. The TG-DTA studies showed that the compound was stable up to 198°C. The spectral characterizations were also carried out.

The crystal structure of 2:1 tetramethylpyrazine picrate was studied by Sawka-Dobrowolska *et al.* (2010). The single crystal X-ray diffraction study revealed that the crystal system of the compound was monoclinic with $P2_1/n$ space group. The spectral and inelastic neutron scattering studies were also characterized. Huilu Wu *et al.* (2010) have reported a V-shaped 2,6-bis (2-benzimidazolyl) pyridine picrate Mn(II) complex. The DNA-binding properties of the two compounds were investigated by electronic absorption spectrum, fluorescence spectrum and viscosity measurements. The single crystal X-ray diffraction study indicated that the synthesized crystal belonged to monoclinic system with $P2_1/c$ space group.

Charge transfer complex, *p*-phenylenediamine picrate was synthesized by Khan *et al.* (2010). The complex exhibited good antifungal and antibacterial activities. The physical parameters of the complex were evaluated by the Benesi-Hildebrand equation. The elemental, spectral, thermal and electronic absorption spectral techniques were also used to characterize the complex.

The single crystal of 1-(diaminomethylene) thiuron-1-ium picrate was grown by Janczak Jan *et al.* (2010). The compound crystallized in monoclinic system with centrosymmetric $C2/c$ space group. The characteristic bands of the NH_2 , NO_2 and $C_{ar}-O$ groups as well as of skeletal vibration were assigned using FTIR and Raman spectral techniques.

A new and efficient organic nonlinear optical crystal L-threoninium picrate was grown by Natarajan *et al.* (2010). The structure of the crystal was monoclinic with non-

centrosymmetric space group $P2_1$. The second harmonic generation efficiency of this material was 43 times greater than that of the standard KDP.

The glycine glycinium picrate crystal was reported by Kai *et al.* [97]. The structure of crystal was monoclinic system with $P2_1/a$ space group. But later Ghazaryan *et al.* (2010) reported the $P2_1/c$ space group instead of $P2_1/a$ space group for the glycine glycinium picrate. No glycine picrates were reported. The SHG effect for the centrosymmetrical species of diglycine picrate was reported by Ghazaryan *et al.* (2011). They have concluded that the SHG effect of the centrosymmetrical species was due to impurities of picric acid.

Basoglu *et al.* (2011)] have studied the quantum chemical calculations of geometrical structure and vibrational wavenumbers of 8-hydroxyquinolinium picrate. The single crystal X-ray analysis showed that the grown crystal belonged to monoclinic system with $C2_1/c$ space group. Theoretical molecular frontier orbital energies of the compound were calculated. Vladimir Stilinovi *et al.* (2011) synthesized a series of 20 picrates of pyridine derivatives and their crystal structures were studied by single crystal X-ray diffraction method. The single crystal X-ray analysis indicated that the most of the pyridinium picrates crystallized in monoclinic crystal systems with $P2_1/c$ space groups.

A new charge transfer complex of 1,10-phenanthroline picrate was synthesized by Khan *et al.* (2011). The complex exhibited good antibacterial and antifungal activities. The single crystal structure analysis suggested that the grown complex belonged to monoclinic system with $P2_1/c$ space group. The spectral and other characterizations were also studied.

Antony Joseph *et al.* (2011) have synthesized an optical crystal of glycine mixed L-valine picrate. Single crystal X-ray

diffraction analysis revealed that the crystal crystallized in orthorhombic system. UV-vis-NIR analysis indicated that the crystal can be used as an NLO material.

The molecular charge complex urea picrate and its third order nonlinear optical properties were investigated by Naseema *et al.* (2011). The complex exhibited good optical limiting at 532 nm with the limiting threshold of 80 mJ/pulse. Thermal properties of the complex were also carried out. UV-visible spectrum indicated that the complex can be used as an NLO material.

Gowri *et al.* (2011) have synthesized a new organic nonlinear optical material, L-tryptophan picrate. The grown material crystallized in orthorhombic system with non-centrosymmetric space group $P2_12_12_1$ as determined by single crystal X-ray analysis. Thermal study indicated that the compound was thermally stable up to 197°C. The SHG efficiency was confirmed by the emission of green light.

The structural, optical, SHG, crystalline perfection and thermal analyses of L-Leucine L-Leucinium picrate crystal were investigated by Bhagavannarayana *et al.* (2011). The crystal system was triclinic with $P2_1$ space group. Its SHG efficiency was 1.5 times greater than that of KDP. Thermal studies revealed that the crystal was stable up to 195°C.

Magesh *et al.* (2011) have synthesized dimethylammonium picrate by slow evaporation solution technique and subsequently by Sankaranarayanan–Ramasamy method. The crystal perfection of the grown crystal was analyzed using High resolution-XRD method. The microhardness study revealed that the crystal belonged to soft material. Lower cut-off wavelength and optical transmission window of the crystal were assessed by UV-vis-NIR and the refractive index of the crystal (001) plane was also found.

A mononuclear Sm(III) tetraethylene glycol picrate was studied by Eny Kusriani *et al.*

(2011). The structure of the complex was triclinic crystal system and the space group was $P\bar{1}$.

A novel noncentrosymmetric crystal, 1,3-dimethylurea dimethylammonium picrate was grown by Anandha Babu *et al.* (2011). It crystallized in orthorhombic system with noncentrosymmetric $Cmc2_1$ space group. The structural perfection of the grown crystals was analysed by High-resolution XRD measurements. The SHG efficiency of the compound was 4 times greater than that of KDP.

A charge transfer complex, 2,6-diaminopyridine picrate was grown by Khan *et al.* (2011). The complex crystallized in triclinic crystal system with $P\bar{1}$ space group. The compound exhibited good antimicrobial activities. Thermal study indicated that the compound was thermally stable up to 135°C. The spectral characterizations were also studied.

Subramaniyan Raja *et al.* (2011) have synthesized the crystalline substance of N,N-diethyl anilinium picrate. The compound crystallized in monoclinic system and the space group was $P2_1/c$. The TG-DTA analysis suggested that the compound was thermally stable up to 144°C. The Vicker's microhardness test showed that compound belonged to soft material. A mononuclear of trietraethylene glycol Eu(III) picrate complex was reported by Saleh *et al.* (2011). The complex crystallized in triclinic system with $P\bar{1}$ space group. The photoluminescence and electroluminescence spectra indicated that all the emissions were due to the characteristic transitions of the Eu(III) ion.

Charge transfer complex formed between norfloxacin or ciprofloxacin with picric acid and 3,5-dinitrobenzoic acid were studied by Refat *et al.* (2011). The single crystal X-ray diffraction investigation revealed that the crystal system of the complex was monoclinic. Thermal analysis indicated that

the compound was thermally stable up to 290°C. Elemental, IR, ¹H NMR and UV-visible characterizations were also made. Anandhi *et al.* (2011) have synthesized the organic single crystal, imidazolium picrate. The single crystal X-ray analysis of the complex indicated the grown crystal belonged to monoclinic crystal system with P₂₁/c space group. The photoluminescence spectrum of the compound showed that it exhibited green emission. Dielectric tensor components were determined theoretically using the DFT theory. The thermal study indicated that the compound was thermally stable up to 235°C.

A new charge transfer complex of 1,10-phenanthroline picrate was studied by Khan *et al.* (2011). The structure of complex was determined by single crystal X-ray diffraction method and found that the complex crystallized in triclinic system with P $\bar{1}$ space group. Other characterizations were also carried out. The antimicrobial activity results indicate that the complex shows good inhibition against various bacteria and fungi.

Gowri *et al.* (2012) reported a new organic NLO material, adenosinium picrate. The crystalline nature of the material was studied by powder X-ray diffraction pattern. The synthesized material crystallized in orthorhombic system with non-centrosymmetric P₂₁₂₁₂₁ space group. The SHG efficiency of the materials was 0.25 times greater than that of KDP. TG-DTA analyses were used to study its thermal properties. Two novel zinc(II) bis(1-ethylbenzimidazol-2-yl)-2-thiapropane picrate complexes were synthesized by Wu *et al.* [(2012) . The single crystal X-ray analysis showed that the complexes crystallized in triclinic systems with P $\bar{1}$ space groups. The DNA binding study results suggested that the complexes exhibited good DNA-binding affinity. The spectral and electrical conductivity characterizations were also carried out.

Santhakumari *et al.* (2012) have studied the semiorganic material, thiosemicarbazide cadmium(II) picrate. The single crystal X-ray analysis showed that compound belonged to triclinic system with P $\bar{1}$ space group. The synthesized compound showed good antibacterial and antifungal activities.

Kusrini *et al.* (2012) have studied a new europium picrate complex, [Eu(Pic)₂(H₂O)(EO₄)](Pic)0.75H₂O. The synthesized complex crystallized in triclinic system with P $\bar{1}$ space group as determined by single crystal X-ray analysis. The energy transfer process from the ligand to the Eu(III) ion was discussed by investigating the excitation and photoluminescence characteristics.

The preparation, crystal and molecular structure as well as vibrational spectra of L-alanine L-alaninium picrate monohydrate crystal were studied by Ghazaryan *et al.* (2012) . The single crystal X-ray analysis showed that the crystal system of the complex was monoclinic with P₂₁ space group. The IR and Raman spectra were also carried out to confirm the various functional groups in the crystal.

The effect of nickel doping on L-valinium picrate single crystal was studied by Russel Raj *et al.* (2012). The TG-DTA studies indicated that the doped crystals exhibited better thermal stability than that of undoped crystal. The single crystal X-ray diffraction analysis suggested that the crystal crystallized in monoclinic system. The SHG efficiency of the pure complex was 60 times higher than that of KDP but for the doped complex the SHG efficiency was 45 times greater than that of KDP.

Jin *et al.* (2012) have investigated four 2-methylquinoline derived supramolecular picrate complexes. The structures of the complexes were determined by single crystal X-ray diffraction analysis. The single crystal X-ray analysis indicated that the crystal systems of the complexes were

triclinic with $P\bar{1}$ space groups. The spectral characterizations were also studied.

The V-shape ligand bis(N-allylbenzimidazol-2-ylmethyl)benzylamine substituted nickel picrate complexes were synthesized by Wu *et al.* (2012). Single crystal X-ray analysis revealed that the complex belonged to triclinic system with $P\bar{1}$ space group. The DNA-binding study indicated that the Ni(II) picrate complex showed good DNA binding mode when compared with ligand.

Yong-Jun Zheng *et al.* (2012) have studied two new circular tetranuclear 2-{NO- [2-(dimethylamino) ethyl]oxamido} benzoate copper(II) 2,2 bipyridine and 1, 10 phenanthroline picrate complexes. The single crystal X-ray diffraction study showed that the complexes crystallized in triclinic system with $P\bar{1}$ space group and monoclinic, $P2_1/n$ space group respectively. The complexes exhibited good DNA affinity. Two 2,6-bis(2-benzimidazolyl)pyridine zinc(II) and cadmium(II) picrate complexes were synthesized by Wu *et al.* (2012). The Zn(II) and Cd(II) complexes crystallized in monoclinic systems with $P2_1/n$ space groups as confirmed by single crystal X-ray diffraction analysis. The DNA-binding properties of the complexes suggested that the Zn(II) complex had more binding affinity than that of Cd(II) complex.

Molecular charge transfer complexes of the tetramethylethylenediamine with picric acid, benzene-1,4-diol, tin(IV) tetrachloride iodine, bromine and zinc chloride were reported by Abdel Majid *et al.* (2012). Thermal studies indicated that the complexes were thermally stable up to 191°C. The complexes exhibited good antibacterial and antifungal activities. The electrical properties, AC conductivity and the dielectric coefficients were also measured.

Muthu *et al.* (2012) studied the single crystal of tetrakis(thiourea) zinc(II) picrate. The single crystal X-ray diffraction study revealed that the crystal belonged to triclinic system with $P\bar{1}$ space group. The diffuse

reflectance spectroscopy was employed to estimate the band gap energy. The crystallinity was studied by powder X-ray diffraction method.

p-Toluidinium picrate crystal was studied by Muthu *et al.* (2012). The UV-visible spectrum indicated that the compound was suitable for optoelectronic applications. The powder XRD patterns of crystal showed that the sample had single phase without detectable impurity. The compound crystallized in monoclinic system with space group $P2_1/c$.

Single crystal growth, spectroscopic, relative SHG efficiency and thermal analyses of 2-aminopyridinium picrate were reported by Shakir *et al.* (2012). The TG-DTA thermal analyses showed that the grown crystal was stable up to 223°C. The single crystal X-ray diffraction method revealed that the crystal system was triclinic with $P\bar{1}$ space group. Crystalline perfection of the grown crystal was assessed by high-resolution XRD. The SHG efficiency of the crystal was 0.15 times greater than that of KDP.

Fleck *et al.* (2012) have reported -alaninium picrate crystal. The structure of the crystal was determined by single crystal X-ray diffraction method. The synthesized crystal crystallized in triclinic system with space group $P\bar{1}$, $Z = 2$. The infrared and Raman spectra of the grown crystal were also studied. Sudharsana *et al.* (2012) have investigated the hydroxyethylammonium picrate crystal. The single crystal X-ray analysis showed that the grown crystal belonged to monoclinic crystal system with centrosymmetrical $P2_1/c$ space group. The Z-scan was carried out to measure the effective third-order nonlinear optical susceptibility, which was 3.24×10^{-3} esu. Optical, mechanical and thermal studies were also carried out.

Bismi Edwin *et al.* (2012) studied the vibrational spectral analysis and quantum

chemical computations of L-prolinium picrate crystal. The vibrational analysis revealed the presence of strong O-H...O and N-H...O interaction between L-prolinium and picrate ions. The equilibrium geometry, various bonding features and harmonic vibrational wave number of the crystal were also investigated.

Adam (2012) studied the charge transfer complexes of procaine hydrochloride with quinol, picric acid and 7,7' 8,8'-tetracyanoquinodimethane. The complex obtained from the picric acid shows moderate inhibition antibacterial and antifungal activities against various bacteria and fungi. The thermal and spectral studies were also used to characterize the complexes.

A good nonlinear optical materials, l-Asparaginium picrate and Co²⁺ doped l-Asparaginium picrate were studied by Russel Raj and Murugakoothan (2012). The doped crystal has high SHG efficiency than undoped crystal when compared KDP. The TG-DTA studies showed that the doped crystal exhibit better thermal stability than pure l-Asparaginium picrate. The single crystal X-ray analysis shows that the doped and undoped crystals were crystallized in monoclinic crystal systems. Other characterizations were also carried out.

Conclusion

A survey of literature on organic picrate complexes reveals the following points clearly. There are many nitrogen containing heterocyclic-picrate complexes to be synthesized and characterized. Among the organic picrate complexes synthesized so far, there are many other physical properties yet to be studied. The complete structural studies for all the picrate complexes synthesized so far are not available in the literature.

Thermal analyses (TG-DTA and DSC) and spectral studies (UV-visible, Emission, Polarized Raman, FTIR and NMR) for many

picrate complexes are not reported. Properties like dielectric, nonlinear optical, mechanical and antimicrobial activity studies of a number of picrate complexes are not studied.

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