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Research Article

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Growth and structural characterization of l-lysine 4-nitrophenolate monohydrate (LLPNP) optical single crystals

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ABSTRACT

The compound LLPNP crystallizes in orthorhombic system, $P2_1\ 2_1\ 2_1$ space group with four molecules in the asymmetric unit. The crystal data for LLPNP is tabled. The lysine molecule (C1-C6/N1/N2/O1/O2) is protonated while the paranitrophenol molecule is deprotonated (C7-C12/N3/O3/O4/O5). The paranitrophenol moiety makes a dihedral angle of 85.87 (9)° with the lysine moiety which shows that they are almost orthogonal to each other. The phenyl ring adopts a planar conformation with C7 atom having a maximum deviation of 0.0013 (14) Å. The oxygen atom O3 attached with the phenyl ring deviates by 0.0004 (1) Å. The nitro group (N3/O4/O5) makes a dihedral angle of 2.63 (1)° with the phenyl ring to which it is attached.

Keywords: l-lysine 4-nitrophenolate monohydrate, Structural characterization, protonated.

INTRODUCTION

For the last few decades the development of potential nonlinear optical (NLO) crystals, generating blue and green lasers by frequency conversion is of great interest among the researchers. Organic NLO materials plays a major role in nonlinear optics as they have fast response, high NLO efficiency and high laser damage threshold compared to inorganic NLO materials[1]. The nonlinear susceptibility of an organic material would be larger when it has donor-acceptor conjugated molecular systems. Moreover, the selection of the type of donor, acceptor and conjugated electron system is a key factor in the molecular engineering and design of organic NLO crystals for particular wavelength conversion. Several novel organic NLO materials with excellent properties have been developed by considering the above factor, such as DAST and other crystals as reported in the literatures[2-5]. Vijayan et al has studied the growth and characterization of benzimidazole and L-alanine organic single crystals[6,7]. Gao et al reported the structural and optical properties of N-(4-nitrophenyl)-N-methyl-2-amino acetonitrile (NPAN) single crystals[8]. L-Lysine is one of the amino acids which give large no of derivatives with organic and inorganic counterpart such as L-lysine acetate [9], L-lysine sulphate [10], L-lysine monohydrochloride [11], L-lysiniumtrifluoro acetate[12] and L-lysine L-tartaric acid[13]. On the other hand, Paranitrophenol totally matches the aforementioned criterion with its electron donor substituent ‘‘–OH’’ and electron acceptor substituents ‘‘–NO_2’’ in which, –OH,–NO_2 and phenyl group form a conjugated molecular configuration. Recently, L-arginine 4-nitrophenolate 4-nitrophenol dihydrate (LAPP) crystal was reported, which has a high second order nonlinear coefficient[14]. Amino acid L-histidine and piperazinium also gave derivative with 4-nitrophenol as recently reported[15]. Large size growth of this family crystal

is difficult and these crystals are highly hygroscopic in nature[16]. The growth and characterization of the above crystal was published by Mahadevan et.al., Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy.

In this paper, an attempt has been made in the present investigation to explain the crystallographic aspects of a new semiorganic material namely L-lysine 4-nitrophenolate monohydrate (LLPNP) by mixing the L-lysine monohydrate and 4-nitrophenol at the equimolar ratio (1:1).

SYNTHESIS AND GROWTH OF LLPNP CRYSTALS

L-lysine monohydrate and 4-nitrophenol were taken in equimolar ratio with excess of water to synthesis the LLPNP material. The calculated amount of L-lysine monohydrate is dissolved in double distilled deionized water under stirring condition. The measured amount of 4-nitrophenol was added with the solution and the vigorous stirring was allowed for more than two hours. The homogeneous solution was filtered to avoid residual solutes and impurities if any and carefully transferred into a crystallizer. The filtered solution was kept in a room temperature and allowed for solvent evaporation. The mechanism of formation of LLPNP is given by the following chemical reaction,

$C_6H_{14}N_2O_2 \cdot H_2O + C_6H_5NO_3 \rightarrow C_{12}\ H_{21}\ N_3\ O_6$

The synthesized products were collected and dissolved again in the de ionized water to prepare a saturated solution. After that the saturated solution was filtered into another crystallizer and kept at room temperature after covering the solution for slow evaporation. After 30 days, yellow colored single crystals of dimension around $12 \times 8 \times 6$ mm^3 have been grown in the solution and crystals were carefully harvested. Photograph of the as-grown LLPNP optical single crystals are shown in **Figure 1.**

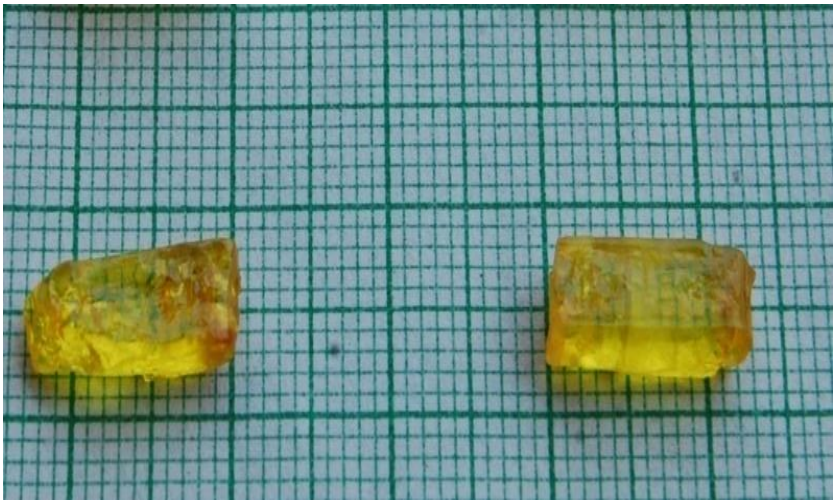

Figure 1 As-grown single crystals of LLPNP

INTENSITY DATA COLLECTION

X-ray diffraction intensity data was collected on Bruker axs SMART APEXII single crystal X-ray diffractometer equipped with graphite monochromated Mo*Kα* (λ=0.7103 Å) radiation and CCD detector. Crystals were cut to suitable size and mounted on a glass fibre using cyanoacrylate adhesive. The unit cell parameters were determined from 36 frames measured (0.5° phi-scan) from three different crystallographic zones and using the method of difference vectors. The intensity data were collected with an average four-fold redundancy per reflection and optimum resolution (0.75 Å). The intensity data collection, frames integration, Lorentz and polarization correction and decay correction were done using *SAINT-NT* (version 7.06a) software. Empirical absorption correction (multi-scan) was performed using *SADABS*[17] program.

Crystal structure was solved by direct methods using *SHELXS-97*[18]. The structure was then refined by the full-matrix least-squares method using *SHELXL-97*[18]. The molecular graphics diagram ORTEP-3 is drawn using PLATON program[19, 20].

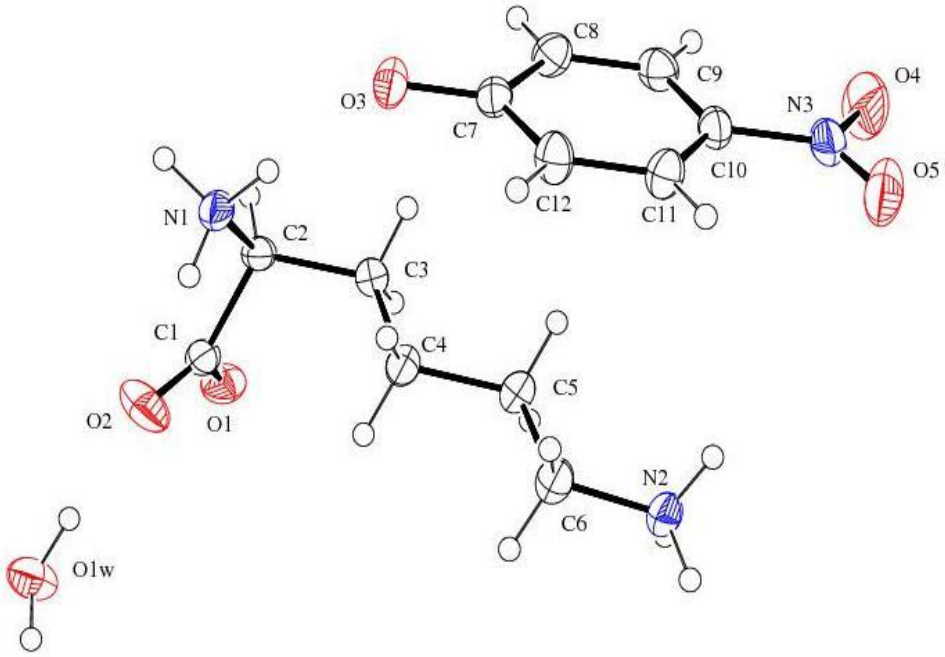

Figure 2: The ORTEP plot of LLPNP with the atom numbering scheme. Displacement ellipsoids are drawn at 30% probability level

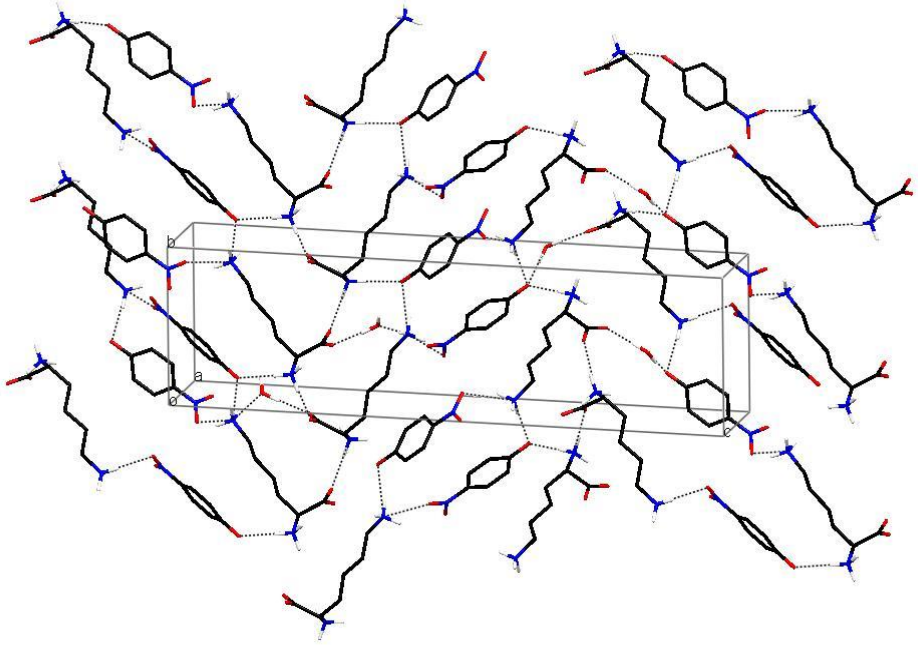

Figure 3: The molecular packing of LLPNP forming a three Dimensional network

Table 1: Crystal data for LLPNP

Parameters	LLPNP
Empirical formula	C_{12} H_{21} N_3 O_6
Formula weight	303.32
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Orthorhombic, P 2_1 2_1 2_1
Unit cell dimensions	a=5.4382(2)Å b=8.5023(4)Å c=30.9204(15)Å
Volume ($Å^3$)	1429.67 (11)
Z, Calculated density (Mg/m^3)	4, 1.409
Absorption coefficient (mm^{-1})	0.113
F(000)	648
Crystal size (mm^3)	0.30 × 0.25 × 0.20
Theta range for data collection	2.48 to 25.49°
Limiting indices	−6≤h≤6, −9≤k≤9, −36≤l≤37
Reflections collected / unique	8813/ 2557 [R(int) = 0.0223]
Completeness to theta (%)	96.4
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2557 / 8 / 223
Goodness-of-fit on F^2	1.019
Final R indices [I>2σ(I)]	R1 = 0.0217, wR2 = 0.0734
R indices (all data)	R1 = 0.0295, wR2 = 0.0751
Largest diff. peak and hole ($e.Å^{-3}$)	0.140 and −0.119

Table 2: Selected bond length for LLPNP (Å)

Atom	Length
C(1)-O(2)	1.2354(19)
C(1)-O(1)	1.2509(19)
C(1)-C(2)	1.5296(18)
C(2)-N(1)	1.4993(19)
C(2)-C(3)	1.5217(19)
C(3)-C(4)	1.514(2)
C(4)-C(5)	1.5160(19)
C(5)-C(6)	1.499(2)
C(6)-N(2)	1.478(2)
C(7)-O(3)	1.3034(16)
C(7)-C(8)	1.409(2)
C(7)-C(12)	1.412(2)
C(8)-C(9)	1.371(2)
C(9)-C(10)	1.384(2)
C(10)-C(11)	1.387(2)
C(10)-N(3)	1.4313(19)
C(11)-C(12)	1.364(2)
N(3)-O(4)	1.224(2)
N(3)-O(5)	1.231(2)

Table 3: Selected bond angle for LLPNP (Å)

Atom	Angle
O(2)-C(1)-O(1)	127.81(14)
O(2)-C(1)-C(2)	117.53(13)
O(1)-C(1)-C(2)	114.62(13)
N(1)-C(2)-C(3)	110.44(11)
N(1)-C(2)-C(1)	111.04(12)
C(3)-C(2)-C(1)	110.39(12)
C(4)-C(3)-C(2)	114.67(11)
C(3)-C(4)-C(5)	111.56(11)
C(6)-C(5)-C(4)	112.16(12)
N(2)-C(6)-C(5)	111.00(12)
O(3)-C(7)-C(8)	122.00(13)
O(3)-C(7)-C(12)	121.64(12)
C(8)-C(7)-C(12)	116.36(12)
C(9)-C(8)-C(7)	121.76(14)
C(8)-C(9)-C(10)	119.60(13)
C(9)-C(10)-C(11)	120.69(13)
C(9)-C(10)-N(3)	119.56(13)
C(11)-C(10)-N(3)	119.75(14)
C(12)-C(11)-C(10)	119.21(14)
C(11)-C(12)-C(7)	122.38(13)
O(4)-N(3)-O(5)	121.93(14)
O(4)-N(3)-C(10)	118.74(16)
O(5)-N(3)-C(10)	119.33(14)

Table 4: Hydrogen Bond Geometry for LLPNP [Å and º]

D-H…A	D-H	H…A	D…A	D-H…A
N(1) --H(1A) ..O(3)	0.914(13)	2.011(13)	2.9222(15)	175.4(15)
N(1) --H(1B) ..O(1)^{i}	0.918(12)	1.915(13)	2.8045(18)	162.7(15)
N(1) --H(1C) ..O(1)^{ii}	0.923(16)	2.512(16)	3.3522(16)	151.5(13)
N(1) --H(1C) ..O(2)	0.923(16)	2.149(16)	2.6689(17)	114.7(13)
O(1W) --H(1W) ..O(2)	0.925(14)	1.783(14)	2.7078(16)	177.6(19)
N(2) --H(2A) ..O(4)^{iii}	0.913(13)	2.316(15)	2.857(2)	117.7(13)
N(2) --H(2A) ..O(5)^{iv}	0.913(13)	2.334(15)	2.9976(19)	129.4(13)
N(2) --H(2B) ..O(3)^{v}	0.920(17)	1.918(16)	2.7980(18)	159.4(19)
N(2) --H(2C) ..O(1W)^{vi}	0.919(12)	1.816(15)	2.6993(19)	160.4(18)
O(1W) --H(2W) ..O(3)^{vii}	0.922(17)	1.783(17)	2.6894(16)	166.8(17)

Symmetry codes: i) x,-1/2+y,1/2-z ii)-1+x,y,z iii) -1/2+x,3/2-y,-z iv) 1/2+x,3/2-y,-z v) x,1+y,z vi) 1-x,1/2+y,1/2-z vii) -x,1/2+y,1/2-z

CONCLUSION

The title compound crystallizes in orthorhombic system, $P2_1\ 2_1\ 2_1$ space group with four molecules in the asymmetric unit (**Figure 2**). The crystal data for LLPNP is given in **Table 1**. The lysine molecule (C1-C6/N1/N2/O1/O2) is protonated while the paranitrophenol molecule is deprotonated (C7-C12/N3/O3/O4/O5). The paranitrophenol moiety makes a dihedral angle of 85.87(9)° with the lysine moiety which shows that they are almost orthogonal to each other. The phenyl ring adopts a planar conformation with C7 atom having a maximum deviation of 0.0013(14) Å. The oxygen atom O3 attached with the phenyl ring deviates by 0.0004 (1) Å. The nitro group (N3/O4/O5) makes a dihedral angle of 2.63(1)° with the phenyl ring to which it is attached. In the crystal, the molecular packing is stabilized by intermolecular N—H…O and O—H…O hydrogen bonds which generate a three dimensional network (**Figure 3** and **Table 2**). Further it is consolidated by intramolecular N—H…O and O—H…O hydrogen bonds. The selected bond length and bond angle is given in **Table 2 and 3**, respectively. The hydrogen bond geometry is given in **Table 4.**

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