Crystal growth and structure of L-methionine L-methioninium hydrogen maleate—a new NLO material

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Abstract
A new organic nonlinear optical (NLO) crystal from the amino acid family, viz., L-methionine L-methioninium hydrogen maleate (LMMM), has been grown by slow evaporation method from aqueous solution. Bulk crystals were grown using submerged seed solution method. The structure was elucidated using the single crystal x-ray diffraction data. The compound crystallized in the space group P2₁ and the unit cell contains a protonated L-methioninium cation and a zwitterionic methionine residue plus a maleate anion. The backbone conformation angles Ψ1 and Ψ2 are in cis and trans configurations for both the methionine and methioninium residues, respectively. Amino and carboxyl groups of the methioninium and methionine residues are connected through N–H⋯O hydrogen bonds leading to a ring R2²(10) motif.

Keywords: L-methionine L-methioninium hydrogen maleate, x-ray diffraction, crystal structure, nonlinear optical material

(Some figures in this article are in colour only in the electronic version)

1. Introduction
Methionine is one of the two sulfur-containing proteinogenic amino acids, the other one being cysteine. The crystal structure of methionine and its different salts have been reported earlier [1–5]. Due to the potential applications of organic nonlinear optical (NLO) materials, lots of research are being carried out to synthesize new organic NLO materials. Salts of maleic acid with amino acids, viz., L-Alaninium maleate [6] and L-Arginine maleate [7] were synthesized and identified as NLO materials and reported recently. In this article, a new NLO material, the molecular structure of L-methionine L-methioninium hydrogen maleate (LMMM), is reported.

2. Experimental
2.1. Crystal growth
LMMM crystals were obtained by slow evaporation of an aqueous solution containing L-methionine and maleic acid (Std. fine, India) in the 2:1 ratio. Optically clear and well-shaped crystals suitable for usage as seed crystals were obtained in a period of few days. Bulk crystals were grown using the seeds in a saturated solution of LMMM in a crystallizer, using submerged seed solution growth method [8]. In this method, the seed crystal was kept at the bottom of the vessel containing the saturated solution. Transparent crystals of size; 13.0 × 8.0 × 5.0 mm³, were obtained in a period of about four weeks (figure 1).
2.2. Second harmonic generation

Since LMMM has crystallized in a non-centrosymmetric space group, a preliminary study of the powder SHG conversion efficiency was carried out with Nd: YAG laser beam of wavelength 1064 nm, using the Kurtz and Perry method \[9\]. A Q-switched Nd:YAG laser beam of wavelength 1064 nm was used with an input power of 10.5 mJ pulse\(^{-1}\), pulse width of 10 ns, the repetition rate being 10 Hz. The crystals of LMMM were ground to a uniform particle size of about 125–150 \(\mu\)m and then packed in capillaries of uniform bore and exposed to the laser radiation. A powder of KDP, with the same particle size, was used as the reference. The output from the sample was monochromated to collect only the second harmonic (\(\lambda = 532\) nm) eliminating the fundamental, and the intensity was measured using a photomultiplier tube. Second harmonic signal of 300 mV was obtained. The standard KDP crystals gave a SHG signal of 330 mV pulse\(^{-1}\) for the same input energy.

2.3. Structure determination

The unit cell parameters and the crystal structure were determined from the single-crystal X-ray diffraction data obtained using a four-circle Nonius CAD4 MACH3 diffractometer (graphite-monochromated, MoK\(\alpha = 0.71073\) Å) at room temperature (293 K). The data reduction was done using XCAD4 \[10\]. The absorption effect was corrected by the method of \(\psi\)-scan \[11\]. The structure solution and refinement were performed using SHELXTL 6.10 \[12\]. The structure was solved by direct methods, and full-matrix least-squares refinements were performed on F\(^2\) using all the unique reflections. All the non-hydrogen atoms were refined with anisotropic thermal parameters. The H atoms which participated in the H-bonds were located from the difference Fourier and refined with isotropic thermal parameters. The H atoms which participated in the H-bonds were located from the difference Fourier and refined with isotropic thermal parameters. All the other H atoms (–CH) were positioned geometrically and refined using a riding model with C–H = 0.97 (–CH) or 0.98 (–CH\(_2\)) Å with U\(_{iso}(H) = 1.2U_{eq}\) (parent C atom).

3. Results and discussions

The molecular structure \[13\] of LMMM with the atom numbering scheme and thermal ellipsoids drawn at 50\% probability is shown in figure 2. Crystal data, experimental conditions and structure refinement parameters are presented in table 1. Selected bond distances, bond angles and torsion angles are listed in table 2. The hydrogen bond geometry \[14\] is given in table 3 and shown in figure 3.

3.1. Conformational features

The asymmetric part of the unit cell contains two crystallographically independent methionine residues (in cationic and zwitterionic forms) and a maleate anion. The zwitterionic and protonated nature of methionine residues are...
Table 1. Crystal data, experimental conditions and structure refinement parameters.

| Property                        | Value                          |
|---------------------------------|--------------------------------|
| Empirical formula               | C_{14}H_{18}N_{2}O_{5}S_{2}    |
| Formula weight                  | 414.49                         |
| Temperature (K)                 | 293(2)                         |
| Wavelength (Å)                  | 0.71073                        |
| Crystal system, space group     | Monoclinic, P2_1 (No. 4)       |
| Unit cell dimensions (Å, °)     | a = 12.981(8), b = 5.326(3)    |
|                                 | c = 15.124(9), α = 90          |
|                                 | β = 114.09(12), γ = 90        |
| Volume (Å³)                     | 954.6(10)                      |
| Number of molecules in the unit cell and calculated density (mg m⁻³) | 2.144                           |
| Absorption Coefficient (mm⁻¹)  | 0.323                          |
| F(000)                          | 440                            |
| Crystal size (mm³)              | 0.21 × 0.18 × 0.15             |
| θ range for data collection (°) | 2.68° to 24.94°                |
| Limiting indices                | 0 ≤ h ≤ 15                     |
|                                 | −1 ≤ k ≤ 6, −17 ≤ l ≤ 16      |
| Reflections collected/unique    | 2355/2252 [R(int) = .0283]     |
| Completeness of the data        | 99.8%                          |
| Refinement method               | Full-matrix least squares on F² |
| Data/restraints/parameters      | 2252/270                       |
| Goodness-of-fit on F²           | 1.050                          |
| Final R indices [1 > σ(I)]      | R1 = 0.0230, wR2 = 0.0609      |
| R indices (all data)            | R1 = 0.0271, wR2 = 0.0634      |
| Absolute structure parameter    | −0.04(6)                       |
| Extinction coefficient          | 0.028(2)                       |
| Largest diff. peak and hole (e Å⁻³) | 0.152 and −0.154              |
| Programs used for molecular graphics | ORTEP-3 for windows,          |
|                                 | PLATON and mercury 1.4.1       |

Table 2. Selected bond distances (Å), bond angles (°) and torsion angles (°).

| Bond/Stem                  | Δ° | Δ° |
|----------------------------|----|----|
| O(1B)–C(11)                |    | 1.283(3) |
| O(1A)–C(11)                | 1.220(3) |
| N(1)–C(12)                 | 1.499(3) |
| O(2A)–C(21)                | 1.230(3) |
| O(2B)–C(21)                | 1.274(3) |
| N(2)–C(22)                 | 1.500(3) |
| O(31)–C(31)                | 1.282(3) |
| O(31)–C(32)                | 1.240(5) |
| C(34)–O(34)                | 1.234(3) |
| C(34)–O(33)                | 1.272(3) |
| O(1A)–C(11)–C(12)–N(1)     | 121.86(18) |
| O(1B)–C(11)–C(12)–N(1)     | 112.00(19) |
| O(2A)–C(21)–C(22)–N(2)     | 121.41(18) |
| O(2B)–C(21)–C(22)–N(2)     | 112.81(19) |
| O(32)–C(31)–C(32)–N(3)     | 118.7(2) |
| O(31)–C(31)–C(32)–N(3)     | 120.0(2) |
| O(34)–C(34)–C(33)–N(4)     | 118.4(2) |
| O(33)–C(34)–C(33)–N(4)     | 120.0(2) |
| O(1A)–C(11)–C(12)–N(1)     | $\Psi^1$ |
| O(1B)–C(11)–C(12)–N(1)     | −174.51(17) |
| N(1)–C(12)–C(13)–C(14)     | 63.0(3) |
| C(12)–C(13)–C(14)–S(1)     | 175.92(15) |
| C(13)–C(14)–S(1)–C(15)     | 71.12(2) |
| O(2A)–C(21)–C(22)–N(2)     | 88.3(3) |
| O(2B)–C(21)–C(22)–N(2)     | −179.2(18) |
| N(2)–C(22)–C(23)–C(24)     | 57.0(3) |
| C(22)–C(23)–C(24)–S(2)     | 162.45(16) |
| C(23)–C(24)–S(2)–C(25)     | −81.9(3) |

Table 3. The hydrogen-bond geometry (Å, °).

| D–H–...A                  | D–H   | H...A      | D–A   | D–A <(DHA) |
|----------------------------|-------|------------|-------|------------|
| O(1B)–H(1B)...O(2B)       | 1.003(5) | 1.437(7) | 2.437(3) | 175(3) |
| N(1)–H(1B)...O(34)        | 0.95(4) | 2.00(4) | 2.95(3) | 171(3) |
| N(1)–(1C)...O(34)         | 0.88(3) | 2.27(3) | 3.11(5) | 162(2) |
| N(1)–(1C)...O(33)         | 0.88(3) | 2.50(2) | 3.23(2) | 141(2) |
| N(1)–(1D)...O(2A)         | 0.86(2) | 1.93(3) | 2.77(9) | 167(2) |
| N(1)–(2B)...O(32)         | 0.93(3) | 2.12(3) | 3.04(6) | 176(2) |
| N(1)–(2D)...O(32)         | 0.83(3) | 2.25(3) | 3.04(6) | 160(3) |
| N(1)–(2D)...O(1A)         | 0.89(3) | 2.00(3) | 2.85(9) | 160(2) |
| N(1)–(33)...H(31)         | 1.18(3) | 1.25(3) | 2.42(2) | 168(2) |

Symmetry transformations used to generate the equivalent atoms:

(i) x, y + 1, z + 1 (ii) x, y, z (iii) −x−1, y + 1/2, −z + 1
(iv) x, y − 1, z (v) −x−1, y − 1/2, −z−1

3.2. Hydrogen bonding interactions

The maleate anion plays a vital role in hydrogen bonding with the amino acid residues. The methionine and methioninium residues are interlinked as dimer, by a strong asymmetric O–H...O hydrogen bond. Also, an unsymmetrical intramolecular hydrogen bond between atom O33 and O31 of the semi-maleate ion is seen through R(7) ring motif. Both the methioninium and methionine residues are involved in the hydrogen bonding with the maleate anion leading to two infinite chains running along the b-axis of the unit cell (figure 4), leading to chain C_{2}(4) motifs [15]. Amino and carboxyl groups of the methioninium and methionine residues are connected through N–H...O hydrogen bonds leading to a ring R_{2}(10) motif. These ring and chain motifs are aggregated along the ac-diagonal of the unit cell leading to alternate hydrophobic and hydrophilic layers. Hydrophobic regions are enriched with the side chain terminal, −S–CH_{3} group, of the methionine residues.
Figure 3. Packing diagram of LMMM viewed down along the b-axis. H-bonds are shown as dashed lines.

Figure 4. A view of chain C_4^1 motif formed through N–H…O hydrogen bonds (dashed lines) of methioninium residue running along the b-axis of the unit cell. Similar chain motif is formed due to the hydrogen bonds of the methionine residue too.

4. Conclusions

The bulk crystals of a new NLO material from the amino acid family viz., L-methionine L-methioninium hydrogen maleate (LMMM) were grown using submerged seed solution method. The SHG efficiency of this material was measured using the Kurtz and Perry method and found to be about 90% of that of the standard KDP crystal. The π–π* electron transitions due to the delocalized π electrons present in the semi-maleate ion and the carboxylate group may be the origin of the nonlinearity of this material. The crystal structure of LMMM was elucidated using the single crystal X-ray diffraction data.

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