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SYNTHESIS, GROWTH, AND CHARACTERIZATION OF SODIUM COORDINATED GLYCINE-NLO MATERIAL

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A new complex of the amino acid glycine has been synthesized by coordination with sodium nitrate. The title complex, $Na(CH_2NH_2COOH)_2NO_3$, crystallizes in the monoclinic space group, Cc, with parameters $a = 14.331(2)$ Å, $b = 5.262(2)$ Å, $c = 9.119(2)$ Å, $\beta = 119.08(1)^\circ$, $V = 600.8(2)$ Å^3, $Z = 4$, F.W. = 159.06, $D_c = 1.758\,Mg.m^{-3}$, $F_{000} = 324$, $\lambda(MoK_\alpha) = 0.71069$ Å, $\mu = 0.228\,mm^{-1}$, $R1 = 0.0481$. The compound exhibits some novel structural features. The optical second harmonic generation conversion efficiency was determined using Kurtz powder technique. It was found to be twice that of Potassium Diortho Phosphate (KDP).

Keywords: crystal structure study of Glycine sodium nitrate complex; NLO studies

INTRODUCTION

NLO materials for optical second harmonic generation (SHG) have received consistent attention for applications in the field of telecommunication, optical computing, optical information processing, optical disk data storage, laser remote sensing, laser driven fusion, color displays, and medical diagnostics in addition to their usual role of extending the limited frequency available from a laser [1–3].

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The basic requirement for a material to generate optical second harmonic frequency is that it must crystallize in a noncentrosymmetric space group. But, to be useful in practical applications, the material must meet a number of other requirements viz., like being transparent at the wavelength of interest and capable of withstanding high optical powers of the lasers. In addition, the crystal must be available in large size and be chemically stable. Although it is difficult to find a material that satisfies most of the requirements, crystals of amino acids are good candidates for NLO applications.

Glycine, which has three polymorphic modifications, is the simplest amino acid. The most stable phase has its molecules arranged in the form of antiparallel double layers. The molecules in each layer are bound by van der Waals forces, and two layers are connected by hydrogen bonds. Because of the layer structure of glycine, its salts with H_2SO_4 [4], $H_2C_2O_4$ [5], and complex with $AgNO_3$ [6], $CaCl_2$ [7], $BaCl_2$ [8], $SrCl_2$ [9], and $CoBr_2$ [10] crystallize in the same centrosymmetric space group, $P2_1/c$.

We have been exploring the possibility of converting glycine into a highly efficient SHG material by forming its complexes with alkali metals. Among the alkali metal complexes of glycine, only the structure of lithium coordination to glycine is reported [11]. Sodium nitrate which forms a complex with glycine crystallizes in noncentrosymmetric space group, *Cc*. In this paper we report the synthesis, crystal growth, characterization, and study of the nonlinear properties of this crystal which is formed by sodium coordination to glycine.

EXPERIMENTAL

Synthesis and Crystal Growth

Because a standard method is not available for the synthesis of $Na(Gly)NO_3$, a method similar to that described in Muller et al. [11] for the synthesis of lithium complex of glycine has been adopted. The preparations were made in standard glassware without the exclusion of atmospheric oxygen. The starting materials were analytical-grade reagents. Glycine (7.5 gm) and sodium nitrate (4.35 gm) were dissolved in double distilled water. The solution was heated on a water bath until the volume was sufficiently reduced. The reaction that leads to the formation of glycine nitrate (GSN) is the following:

$$2NH_2CH_2COOH + NaNO_3 \rightarrow Na(NH_2CH_2COOH)_2NO_3.$$

Single crystals of glycine sodium nitrate were grown by slow evaporation technique. The crystals were generally aggregates, but well-formed crystals were trigonal pyrmidal. The new crystal was formulated as $Na(Gly)_2NO_3$, which was confirmed by elemental analysis.

Structure Determination

The X-ray diffraction data of the GSN crystal of approximate dimensions $0.2 \times 04 \times 0.5\,\text{mm}^3$ was obtained on Rigaku AFC7S diffractometer with graphite monochromated (MoK_α) radiation. Sixhundred ninety three unique reflections were collected in the 2θ range 6.5°–54.10° with ω-2θ scan technique at room temperature and reduced using teXsan [12] data reduction program. Lorentz and polarization corrections were applied. The structure was solved by direct methods (SHELXS-97) [13] and refined by least squares method (SHELXL-97) [14]. The details are listed in Table 1.

TABLE 1 Crystal Data and Structure Refinement of GSN

Empirical formula	C2 H4 N2 NaO5
Formula weight	159.06
Temperature	293(2) K
Wavelength	0.71069 Å
Reflns. for cell determination	25
θ range for above	12.05–16.48°
Crystal system	Monoclinic
Space group	Cc
Cell dimensions	$a = 14.331(2)$ Å $b = 5.262(2)$ Å $c = 9.118(2)$ Å $\beta = 119.081(9)°$
Volume	600.8(2) Å^3
Z	4
Density (calculated)	1.758 Mg/m^3
Absorption coefficient	0.228 mm^{-1}
F_{000}	324
Crystal size	$0.2 \times 0.4 \times 0.5\,\text{mm}^3$
θ range for data collection	3.25° to 27.05°
Index ranges	$0 \le h \le 18$ $0 \le k \le 6$ $-11 \le l \le 10$
Reflections collected	1231
Independent reflections	1088 (R(int) = 0.012)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	693/2/92
Goodness-of-fit on F^2	1.045
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0478, wR2 = 0.1522$
R indices (all data)	$R1 = 0.0481, wR2 = 0.1529$
Absolute structure parameter	−0.2(9)
Extinction coefficient	0.71(6)
Largest diff. peak and hole	0.326 and −0.423 e.A^{-3}

NLO Property

Quantitative measurement of the conversion efficiency of the crystals was made using the powder technique developed by Kurtz and Perry [15]. The crystal was ground into powder and densely packed between two transparent glass slides. An Nd: YAG laser beam of wavelength 1064 nm was made to fall normally on the sample cell. The transmitted fundamental wave was absorbed by a $CuSO_4$ solution, and the second harmonic signal was detected by a photomultiplier tube and displayed on a storage oscilloscope. A KDP crystal powdered to the identical size was used as the reference material in the SHG measurement. The SHG conversion efficiency was found to be two times that of KDP. Higher efficiencies are expected to be achieved by optimizing the phase matching angle.

Various theoretical models have been proposed to explain and predict the nonlinear optical properties of crystals: the anharmonic vibronic oscillator model [16], the charge transfer model [17], the ionic group theory [18], and so on [19]. Among them, the ionic group theory can be used to explain the nonlinearity in the present complex. According to this theory, the anionic group accounts for the nonlinearity of the complex. The anionic group must be a planar noncentrosymmetric system with -ve character and a lone pair of electrons. Based on this theory, it may be concluded that the anionic group, NO^{-}_{3}, must be one of the origins of the nonlinear properties in GSN. Similar nonlinear effects are reported in the case of $K_2Ln(NO_3)_5{\cdot}2H_2O$ [20].

RESULTS AND DISCUSSION

The final positional coordinates with equivalent isotropic temperature factors for all nonhydrogen atoms are given in Table 2. Anisotropic thermal

TABLE 2 Atomic Coordinates and Equivalent Thermal Parameters of the Nonhydrogen Atoms

Atom	x	y	z	U_{eq}
Na10	0.0388(1)	0.2565(3)	0.2496(2)	0.0421(6)
O1	−0.1446(2)	0.2001(7)	0.1048(4)	0.0466(8)
N2	−0.2440(3)	−0.3031(7)	−0.2046(4)	0.0362(8)
O3	0.2260(3)	0.3139(6)	0.3383(4)	0.0500(9)
N4	0.0454(3)	0.2486(6)	−0.0765(5)	0.0361(8)
C5	−0.1799(3)	−0.1945(8)	−0.0354(5)	0.0398(9)
C6	−0.2012(3)	0.0888(6)	−0.0322(5)	0.0341(8)
O7	0.0551(3)	0.7532(7)	0.2936(5)	0.541(1)
O8	0.0533(4)	0.0487(8)	0.0007(4)	0.059(1)
O9	0.0290(4)	0.4548(8)	−0.0257(5)	0.065(1)

parameters (U_{ij}) for the nonhydrogen atoms are listed in Table 3. Tables 4 and 5 give bond distances and angles of nonhydrogen atoms, respectively.* ORTEP [21] of the molecule with 50% probability is shown in Figure 1. Figure 2 shows the packing of the molecule.

In GSN, sodium is coordinated to eight oxygen atoms, forming a dodecahedron. This is a new feature not found in the glycine complexes reported thus far [4–9]. Six of the oxygen atoms belong to three bidentate

TABLE 3 Anisotropic Thermal Parameters of the Nonhydrogen Atoms

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na10	0.0332(8)	0.0487(10)	0.0365(10)	−0.0025(5)	0.0108(7)	−0.0033(5)
O1	0.0368(17)	0.0526(16)	0.0458(17)	−0.0062(11)	0.0165(14)	−0.0146(13)
N2	0.0358(15)	0.0335(13)	0.0367(15)	−0.0014(11)	−0.0155(12)	−0.0052(12)
O3	0.0384(15)	0.0374(13)	0.0503(18)	0.0007(11)	0.0028(13)	−0.0006(12)
N4	0.0390(19)	0.0405(18)	0.0290(15)	0.0022(11)	0.0166(14)	0.0014(9)
C5	0.038(2)	0.0367(17)	0.0334(15)	0.0027(15)	0.0079(14)	0.0008(15)
C6	0.0249(12)	0.0361(15)	0.0384(14)	−0.0022(12)	0.0131(11)	−0.0016(14)
O7	0.049(2)	0.081(3)	0.0381(17)	0.0078(13)	0.0266(16)	0.0046(11)
O8	0.073(2)	0.0469(17)	0.0475(17)	−0.0016(16)	0.0209(16)	0.0139(14)
O9	0.092(3)	0.0511(19)	0.0548(18)	0.0161(19)	0.0373(19)	−0.0043(16)

TABLE 4 Bond Lengths (Å)

Atoms	Length	Atoms	Length
Na10-O1	2.317(4)	O1-C6	1.256(5)
Na10-O3	2.415(4)	N2-C5	1.474(5)
Na10-O9#1	2.608(5)	O3-C6#4	1.244(5)
Na10-O8	2.617(5)	N4-O8	1.239(5)
Na10-O7	2.637(4)	N4-O9	1.246(5)
Na10-O9	2.658(5)	N4-O7#5	1.258(5)
Na10-O7#2	2.672(4)	N4-Na10#5	3.026(4)
Na10-O8#3	2.720(5)	C5-C6	1.525(5)
Na10-N4	3.021(4)	C6-O3#6	1.244(5)
Na10-N4#1	3.026(4)	O7-N4#1	1.258(5)
O7-Na10#7	2.672(4)	N2-H5A..O3	2.669(4)
O8-Na10#8	2.720(5)	N2-H5B..O3#1	2.779(4)
O9-Na10#5	2.608(5)	C5-H6A..O7	3.255(4)

Symmetry transformations used to generate equivalent atoms:
$\#1 = (x, -y+1, z+1/2), \#2 = (x, y-1, z), \#3 = (x, -y, z+1/2)$
$\#4 = (x+1/2, -y+1/2, z+1/2), \#5 = (x, -y+1, z-1/2)$
$\#6 = (x-1/2, -y+1/2, z-1/2), \#7 = (x, y+1, z)$

*Complete data have been deposited at CSD, reference #CSD 197781.

TABLE 5 Bond Angles (°)

Atoms	Angle	Atoms	Angle
O1-Na10-O3	167.1(2)	O8#3-Na10-N4	142.6(1)
O1-Na10-O9#1	92.5(1)	O1-Na10-N4#1	98.4(1)
O3-Na10-O9#1	98.0(2)	O3-Na10-N4#1	88.3(1)
O1-Na10-O8	89.9(1)	O9#1-Na10-N4#1	24.1(1)
O3-Na10-O8	78.4(1)	O8-Na10-N4#1	144.9(1)
O9#1-Na10-O8	169.0(1)	O7-Na10-N4#1	24.4(1)
O1-Na10-O7	101.9(1)	O9-Na10-N4#1	97.5(1)
O3-Na10-O7	79.8(1)	O7#2-Na10-N4#1	142.8(1)
O9#1-Na10-O7	48.5(1)	O8#3-Na10-N4#1	95.6(1)
O8-Na10-O7	120.5(1)	N4-Na10-N4#1	121.31(8)
O1-Na10-O9	89.3(2)	C6-O1-Na10	129.2(2)
O3-Na10-O9	78.9(1)	C6#4-O3-Na10	130.7(3)
O9#1-Na10-O9	121.0(7)	O8-N4-O9	120.7(5)
O8-Na10-O9	48.3(1)	O8-N4-O7#5	120.4(4)
O7-Na10-O9	73.4(1)	O9-N4-O7#5	118.9(4)
O1-Na10-O7#2	87.2(1)	O8-N4-Na10	59.4(3)
O3-Na10-O7#2	94.1(1)	O9-N4-Na10	61.3(3)
O9#1-Na10-O7#2	119.6(1)	O7#5-N4-Na10	176.0(3)
O8-Na10-O7#2	71.2(1)	O8-N4-Na10#5	176.8(3)
O7-Na10-O7#2	164.7(2)	O9-N4-Na10#5	58.8(3)
O9-Na10-O7#2	119.4(1)	O7#5-N4-Na10#5	60.2(2)
O1-Na10-O8#3	90.3(1)	Na10-N4-Na10#5	119.7(1)
O3-Na10-O8#3	100.0(1)	N2-C5-C6	111.7(3)
09#1-Na10-O8#3	72.2(1)	O3#6-C6-O1	126.2(4)
O8-Na10-O8#3	118.5(7)	O3#6-C6-C5	117.9(3)
O7-Na10-O8#3	119.5(1)	O1-C6-C5	115.9(4)
O9-Na10-O8#3	166.8(1)	N4#1-O7-Na10	95.4(2)
O7#2-Na10-O8#3	47.4(1)	N4#1-O7-Na10#7	96.1(2)
O1-Na10-N4	90.4(1)	Na10-O7-Na10#7	164.7(2)
O3-Na10-N4	76.7(1)	N4-O8-Na10	96.5(3)
O9#1-Na10-N4	145.1(1)	N4-O8-Na10#8	94.3(3)
O8-Na10-N4	24.0(1)	Na10-O8-Na10#8	166.0(2)
O7-Na10-N4	96.9(1)	N4-O9-Na10#5	97.1(3)
O9-Na10-N4	24.3(1)	N4-O9-Na10#5	94.4(3)
O7#2-Na10-N4	95.3(1)	Na10#5-O9-Na10	166.4(2)
N2-H5A..O3	104.0(4)		
N2-H5B..O3#1	140.3(4)		
C5-H6A..O7	130.9(4)		

Symmetry transformations used to generate equivalent atoms:
$\#1 = (x, -y+1, z+1/2), \#2 = (x, y-1, z), \#3 = (x, -y, z+1/2)$
$\#4 = (x+1/2, -y+1/2, z+1/2), \#5 = (x, -y+1, z-1/2)$
$\#6 = (x-1/2, -y+1/2, z-1/2), \#7 = (x, y+1, z)$
$\#8 = (x, -y, z-1/2)$

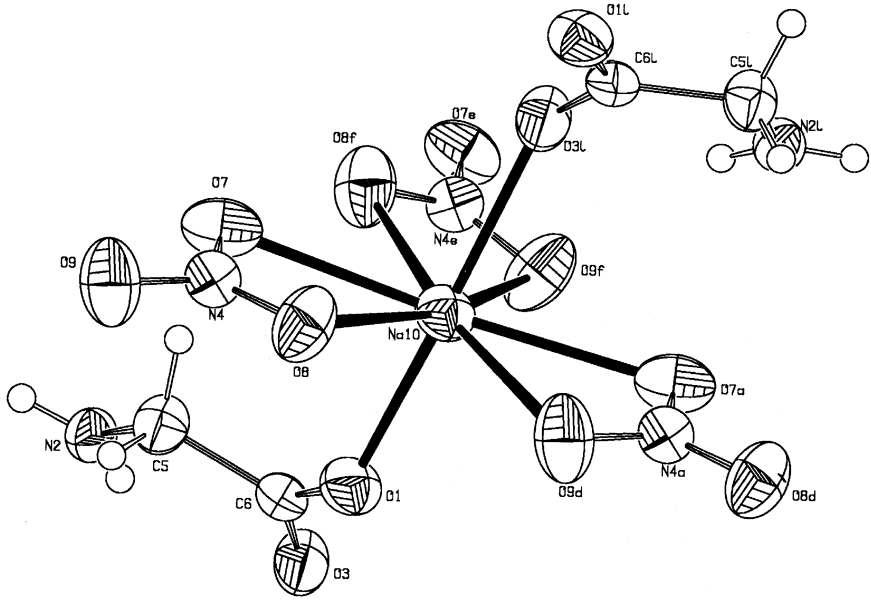

FIGURE 1 ORTEP of the molecule with 50% probability.

nitrate groups, and two are from the carboxylate groups of two different but crystallographically equivalent glycine molecules. Sodium cations bridge the glycine molecules, forming a linear chain. These linear chains are three-dimensionally connected through $NaNO_3$ linkages.

The glycine molecule exists as zwitter-ion in GSN. This is evident from the fact that the C-O distances and the bond angles around the carbon atom of the carboxylate group have values expected for such a configuration. The dimensions of glycine molecule are similar to those found in other glycine complexes.

Free nitrate group is a planar anion with a threefold symmetry axis. In the present complex, the symmetry is distorted due to its coordination with sodium. This is evident from the fact that O-N-O interbond angles of N1 and N2 nitrate groups in GSN show a small deviation from 120°, and all the N-O distances are unequal.

The hydrogen bonding scheme is based on the distances and angles obtained with stereochemically fixed H positions. Only one oxygen atom belonging to the carboxylate group of glycine forms hydrogen bond with the neighboring glycine molecule. The glycine molecules are linked through a head-to-tail hydrogen bond sandwiched between the $NaNO_3^-$ layers. There is no intramolecular H bonding seen, although intermolecular H

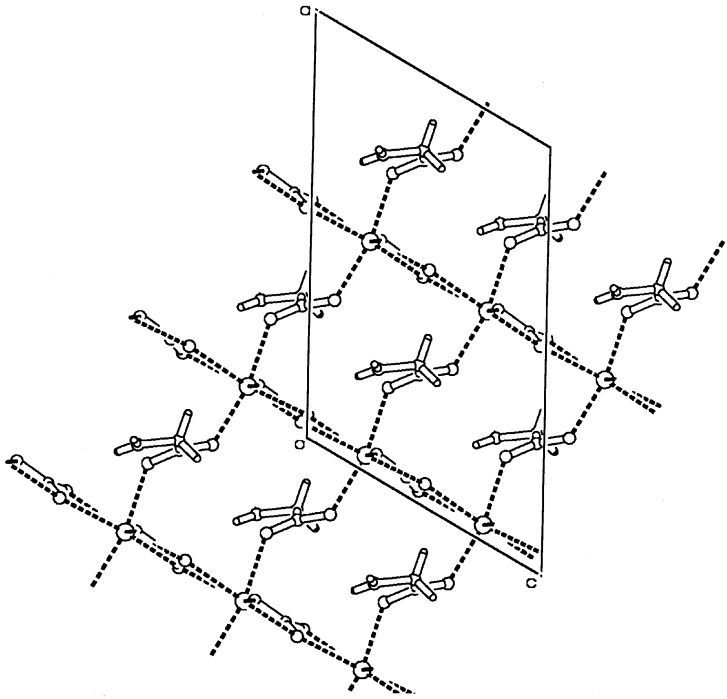

FIGURE 2 Packing of the molecules down *b* axis.

bonding in N2-H5A..O3, N2-H5B..O3, and C5-H6A..O7 exists (Tables 4 and 5).

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