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A Novel TGS-like Inorganic–Organic Hybrid and a Preliminary Investigation of Its Possible Ferroelectric Behavior

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The homochiral inorganic–organic hybrid compound $(H_3NHPA)(SnCl_3)_2(H_2O)_3$ [**1**, (*S*)-4-(4′-aminophenyl)-2-aminobutanoic acid diammonium trichloride stannite triaqua] has a TGS (triglycine sulfate)-like structure. Preliminary investigation suggests a possible ferroelectric behavior with a saturation spontaneous polarization (P_s) of ca. 3.5 $\mu C \cdot cm^{-2}$, which is slightly greater than that of TGS ($P_s = 3.0\ \mu C \cdot cm^{-2}$).

Many solid-state physical properties, such as pyroelectricity, piezoelectricity, ferroelectricity, nonlinear optical second harmonic generation (SHG), and triboluminescence, are found only in noncentrosymmetric bulk materials.[1−3] Among these properties, ferroelectric behavior is the most important and useful, and it is of great interest because it is possible to rapidly switch between different states through the application of an external electric field.[4] Ferroelectric materials may find applications in electric-optical devices, information storage, switchable NLO devices, and light modulators, and these applications are important for optical computing, and other future technologies.[5] One well-known ferroelectric materal is TGS (triglycine sulfate). In this sulfate salt, the amino acid exists in two different forms, as a zwitterion and a cation, which are present in a 1:2 ratio. Strong hydrogen bonds in the crystal packing of TGS play an important role in its spontaneous polarization.[6] The synthesis of new ferroelectric materials is particularly challenging due to the strict requirements that a compound needs to crystallize in noncentrosymmetric space groups belonging to one of 10 polar point groups (C_1, C_2, C_s, C_{2v}, C_4, C_{4v}, C_3, C_{3v}, C_6, C_{6v}). Furthermore, strong H-bonds like those in TGS in the solid-state structures are desirable. Recently, a hybrid inorganic−organic ferroelectric compound containing an amino group attracted considerable attention because of its largest spontaneous polarization. The structure shares similarities with TGS.[6c,7]

In our preparation of (*S*)-4-(4′-aminophenyl)-2-aminobutanoic acid by the reduction of (*S*)-2-amino-4-(4′-nitrophenyl)butyric acid [NOHPA] in the presence of $SnCl_2$ and HCl, we isolated $[NH_3C_6H_4(CH_2)_2(CH)(NH_3)COOH]_2(SnCl_3)_2(H_2O)_3$ [$(H_3NHPA)(SnCl_3)_2\ (H_2O)_3$, **1**, Scheme 1]. We discovered that **1** crystallizes in a polar point group (C_2), a prerequisite for a ferroelectric compound. Herein we report

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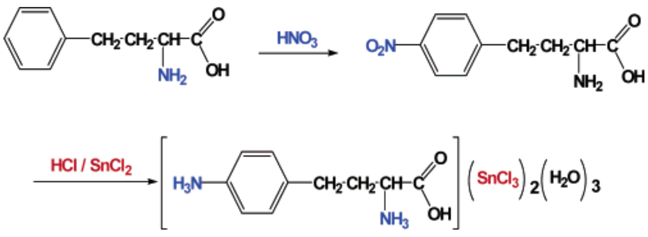
Scheme 1



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its synthesis, solid-state structure, and preliminary investigations of its possible ferroelectric properties.

1 is a yellow compound, and suitable crystals were obtained after the mother liquor was placed in a freezer for 3 days.[8] The absence of the nitro group (present in NOHPA) was indicated by the IR spectrum, which was also consistent with the reduction of the nitro group to an amino group upon addition of $SnCl_2$−HCl. To the best of our knowledge, **1** is the first crystallographically characterized trichlorostannite salt of an amino acid.[9] The structure of **1** was revealed by an X-ray single crystal diffraction investigation. The asymmetric unit is presented in Figure 1.[10] There are two crystallographically unique $SnCl_3^-$ anions which share a similar Sn(II) coordination environment which may be best described as pseudo-trigonal pyramidal. If longer Sn−Cl interactions (Sn···Cl: 3.666 Å) are taken into account, then the Sn lies at the center of a distorted octahedron which is similar to that found in $[Sn_2(Pz)_3]$−$[SnCl_3]$ (Pz = 3,5-dimethylpyrazol-1-yl).[11]

Interestingly, the reduction product of NOHPA is a cation, with both amino groups existing as ammonium groups and the carboxylate group protonated. The cation with the NH_3^+ group on the aliphatic chain and the free carboxylic acid in **1** resembles the two nonzwitterionic amino acids in TGS, which play an important role in spontaneous polarization.[7]

In **1**, both ammonium groups participate in a number N−H···Cl hydrogen bonds with $SnCl_3^-$ anions. The N···Cl separations are in the range 3.297(2) to 3.330(2) Å. These H-bonding interactions result in the formation of a three-dimensional pillar-layered network (Figure 2 and Figure 2S (Supporting Information)). Water molecules participate in two additional, strong hydrogen bonds that extend to the carboxylic acid and the aromatic amino group. The O···O and N···O separations are 2.561(2) and 2.694(2) Å, respectively. There is also direct hydrogen bonding between neighboring amino acids (N2−H2D···O1 2.894 Å) which results in the formation of chains involving only amino acids that extend in the *b* direction.

Given that the product **1** crystallizes in a chiral and polar space group (*I*2), its optical properties were investigated. Preliminary studies of powdered sample indicate that **1** is SHG active with a response of approximately 0.8 times than that of urea.[12] The space group *I*2 is associated with the point group C_2, one of the 10 polar point groups required for ferroelectric behavior. Experimental results indicate that **1** probably displays ferroelectric behavior.[13] Figure 3 clearly

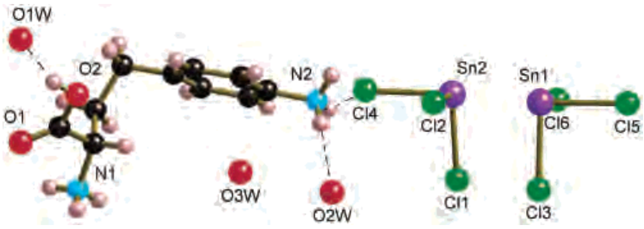

Figure 1. The asymmetric unit of $[NH_3C_6H_4(CH_2)_2(CH)(NH_3)COOH]_2(SnCl_3)_2(H_2O)_3$ showing some of the many H-bonds between the anions and cations. Selected bond lengths [Å] and angles [deg]: Sn1−Cl1 2.4818(15), Sn1−Cl2 2.5464(16), Sn1−Cl3 2.5402(14), Sn2−Cl4 2.5208(13), Sn2−Cl5 2.5312(13), Sn2−Cl6 2.5417(16); Cl1−Sn1−Cl2 91.28(7), Cl1−Sn1−Cl3 94.56(7), Cl2−Sn1−Cl3 88.25(5), Cl4−Sn2−Cl5 91.06(5), Cl4−Sn2−Cl6 88.01(5), Cl5−Sn2−Cl6 89.27(5).

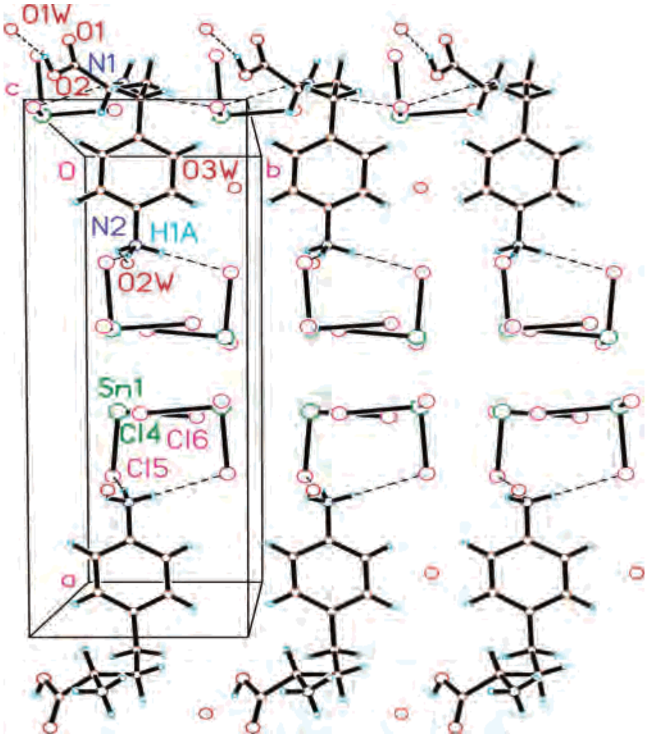

Figure 2. 3D network representation of $[NH_3C_6H_4(CH_2)_2(CH)(NH_3)COOH]_2(SnCl_3)_2(H_2O)_3$.

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(8) Preparation of $C_{10}H_{22}Cl_6N_2O_5Sn_2$ (**1**): Under vigorous stirring, 11.2 g (50 mmol) of 2-amino-4-(4′-nitrophenyl)butyric acid was added to a solution of 34.1 g (152 mmol) of stannous chloride crystals in 47 mL of concentrated hydrochloric acid at 5 °C. After 4 h, the reaction mixture was cooled to about 2 °C and then filtered. The filtrate was placed in a freezer for 3 days. Yellowish crystals were obtained. The yield (3.50 g) of **1** was about 10% based on 2-amino-4-(4′-nitrophenyl)butyric acid while 2-amino-4-(4′-aminophenyl)butyric acid was about 5.2 g. Anal. Calcd for $C_{10}H_{22}Cl_6N_2O_5Sn_2$ (**1**): C 36.58; H 3.05; N 35.56. Found: C 36.47; H 3.11; N 35.31. IR spectrum (KBr, cm^{-1}) of **1**: 3539(s), 3456(s), 3065(s br), 2927(w), 2578(w), 1718(s) 1604(s), 1570(w), 1492(s), 1450(w), 1342(w), 1252(w), 1229(m), 1203(w), 1125(w), 1103(w), 1078(w), 1021(w), 998(w), 976(w), 940(w), 878(w), 819(w), 782(w), 746(w), 706(w), 634(w), 569(w), 522(w), 488(w), 467(w).

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(10) Crystal data for **1**: $C_{10}H_{22}Cl_6N_2O_5Sn_2$, $M = 700.38$, monoclinic, *I*2, $a = 18.3225(10)$ Å, $b = 6.2068(3)$ Å, $c = 20.3289(11)$ Å, $\beta = 94.7870(10)°$, $\alpha = \gamma = 90.00°$, $V = 2303.8(2)$ Å^3, $Z = 4$, $D_c = 2.019$ Mg m^{-3}, $R_1 = 2.92\%$, $wR_2 = 8.99\%$. $T = 293$K, $\mu = 2.885$ mm^{-1}, $S = 0.749$, Flack value = −0.01(3). The structure was solved with direct methods using the program SHELXTL (Sheldrick, 1997). All the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using full-matrix least-squares procedures. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent carbon atoms. The final difference Fourier map was found to be featureless.

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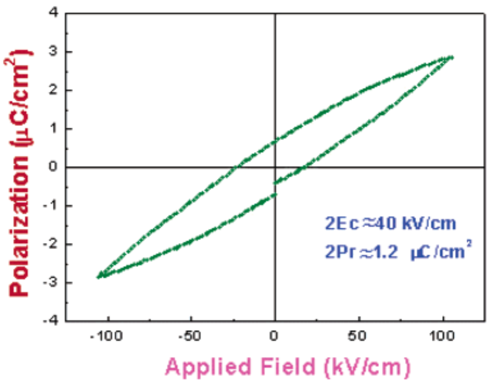

Figure 3. An electric hysteresis loop of a pellet of powders of $[NH_3C_6H_4\text{-}(CH_2)_2(CH)(NH_3)COOH]_2(SnCl_3)_2(H_2O)_3$ was observed by the Virtual Ground Mode using an RT6000 ferroelectric tester at room temperature.

shows there is an electric hysteresis loop which is a typical ferroelectric feature with a remanent polarization (P_r) of ca. 0.60 μC·cm^{-2} and coercive field (E_c) of 20 kV·cm^{-1}. The saturation spontaneous polarization (P_s) of **1** is ca. 3.5 μC·cm^{-2}. In comparison, a P_s of 3.0 μC·cm^{-2} was reported for ferroelectric TGS.[7] It is interesting to note that both **1** and TGS contain protonated amino groups that participate in extensive hydrogen bonding. To the best of our knowledge, **1** represents the first example of inorganic−amino acid hybrid compounds that exhibit possible ferroelectric behavior.

1, which consists of trichloride stannite(II) acting as an anion, and an amino acid as a cation, possesses a TGS-like structure with possible ferroelectric properties. This work suggests a new avenue to functional materials through in situ crystal engineering.[14]

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Supporting Information Available: X-ray CIF files. Figures depicting a space-filling diagram of **1** and a 3D representation of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) The measurement of SHG responses: Approximate estimations of the second-order nonlinear optical intensity were obtained by comparison of the results obtained from a powdered sample (80−150 μm diameter) in the form of a pellet (Kurtz powder test[15]) with that obtained for urea. A pulsed Q-switched Nd:YAG laser at a wavelength of 1064 nm was used to generate the SHG signal. The backward scattered SHG light was collected using a spherical concave mirror and passed through a filter that transmits only 532 nm radiation (the measurement results were obtained by the average value of four times).

(13) The measurement of electric hysteresis loop: The ferroelectric property of solid-state sample was measured by a powdered sample in the form of a pellet using an RT6000 ferroelectric tester (the manufacturer is Radiant Technologies[16]) at room temperature while sample was immerged in insulating oil. The electric hysteresis loop was observed by Virtual Ground Mode (the measurement is ac, the frequency is ca. 4.5−10 Hz). Sometimes the measurement failed due to electric current leakage when the sample was in a KBr pellet. The sample in a thin film may be well measured.

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