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NATURAL SCIENCES

UDK 548.3

NONLINEAR OPTICAL (NLO) MATERIALS: SYNTHESIS, CRYSTAL STRUCTURE AND CHARACTERIZATION OF A NEW ORGANIC–INORGANIC HYBRID MATERIAL 4-(2-AMMONIOETHYL)MORPHOLIN-4-IUM HEXACHLOROSTANNATE(IV).

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Abstrakt. 4-(2-ammonioethyl)morpholin-4-ium hexachlorostannate(IV) formed a nonlinear optical material. The molecula obtained nonlinear optical material(NLO)=$(2a4mh)_2SnCl_6$·4-(2-ammonioethyl)morpholin-4-ium hexachlorostannate(IV)**.** In all the crystal structures presented, cations and anions are arranged alternatively to form chain and ring hydrogen-bonding patterns consisting of weak unconventional N−H•••Cl hydrogen bonds. The compound was first analyzed using single-crystal X-ray diffraction to determine its crystal structure. Subsequently, FTIR (Fourier-transform infrared spectroscopy) and UV-visible absorption spectroscopy studies were conducted to provide insights into the compound's chemical composition and electronic transitions. Nonlinear optical materials were studied by Hirshfield surface analysis and crystal void parts and Elemental analysis.

Keywords: 4-(2-ammonioethyl)morpholin-4-ium hexachlorostannate(IV); Single crystal; Hydrogen bond; Elemental analysis.

Introduction. Organic–inorganic hybrid materials are attracting growing interest for their ability to combine the electronic, magnetic, and thermal stability of inorganic frameworks with the fluorescence and structural versatility of organic molecules[1-3]. Recently, organic–inorganic metal halides have gained significant attention due to their structural diversity and unique properties, such as thermal stability, magnetic behavior, optical activity, and

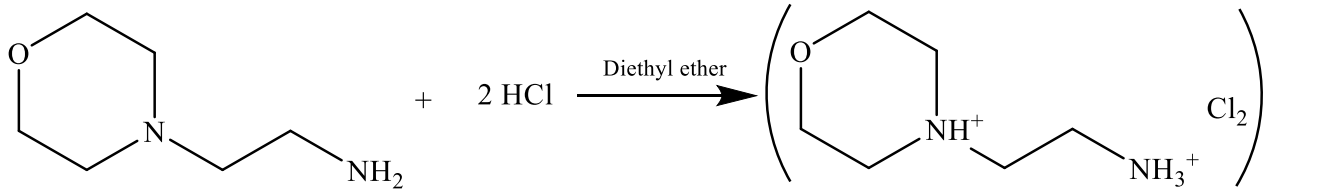
luminescence. Designing hybrid compounds with N-----H bonds is crucial for exploring their potential[4-5]. Materials based on substituted ammonium complexes with halogenated metals (e.g., Hg, Cd, Sn, Cu) exhibit particularly interesting physical properties[6-7]. Sn(II) compounds are a promising class of materials with unique structural features, driven by the inert-pair effect in subvalent Sn(II) atoms[8-9]. Organic-inorganic hybrid materials incorporating pyridine and its derivatives have attracted significant interest due to their photochemical properties[10]. Here, we report the synthesis, crystal structure, and comprehensive characterization of a new organic material 4-(2-ammonioethyl)morpholin-4-ium hexachlorostannate(IV), including spectroscopic (FT-IR, optical, photoluminescence, CP/MAS –NMR), thermal, and optical studies[11-14].

Experimental.

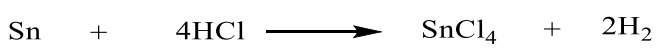
Synthesis of 4-(2-ammonioethyl)morpholin-4-ium hexachlorostannate(IV).

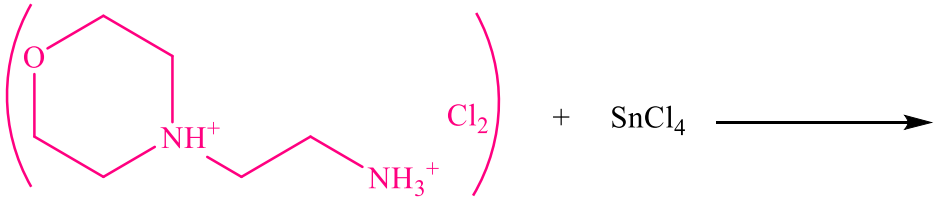
Synthesis: The initial compounds 2-morpholinoethan-1-amine. All reagents and solvents used in the synthesis were of reagent grade and employed without additional purification. Yellow powder 2-morpholinoethan-1-amine [Aldrich, purum > 98% (NT)], (0.152g 10 mM) and hydrochloric acid (Aldrich, 35 % in H_2O, 99.95%), (2 mL) were mixed in diethyl ether (10 mL) at room temperature to form a 4-(2-ammonioethyl)morpholin-4-ium chloride precursor solution. The solution was heated to 60 ^{0}C and kept at this temperature for 10 min. Upon cooling, 4-(2-ammonioethyl)morpholin-4-ium chloride precipitated in the solution. The precipitate was then washed with diethyl ether and dissolved in ethanol. Tin shots, weighing 0.118 g (5 mM), were dissolved in 5 mL of 37 % hydrochloric acid at room temperature over seven hours to produce form **tin chloride** ($SnCl_4$). The tin chloride solution was added to the freshly prepared ethanolic solution of the dichlorine, 4-(2-ammonioethyl)morpholin-4-ium salt precursor while continuously stirring (Scheme-1).

The solution was placed in a thermostat at 25°C for 16-20 days, resulting in the formation of a new crystal.

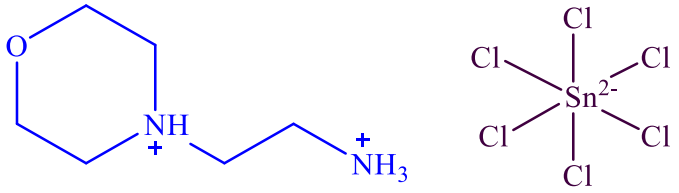


2-morpholinoethan-1-amine dichlorine, 4-(2-ammonioethyl)morpholin-4-ium salt





dichlorine, 4-(2-ammonioethyl)morpholin-4-ium salt



4-(2-ammonioethyl)morpholin-4-ium hexachlorostannate(IV)

(Scheme-1). Synthesis of 4-(2-ammonioethyl)morpholin-4-ium hexachlorostannate(IV).

Single crystal X-ray structure analysis.

The intermolecular hydrogen bonds and hydrogen bonds in the molecule are between the N1-H atom in 2-methyl 4-nitro aniline and the Cl2 and Cl3 atoms in $SnCl_4$. The intermolecular bond is N2-H•••Cl1 and N2-H•••Cl2 occurs between Cl2 and between N1-H•••H-O hydrogen bonds. The intermolecular bond is N2-H•••Cl1 distance is 2.579 Å and distance of N2-H•••Cl2 is 2.883 Å. The valence angle of Cl-Sn-Cl in the $SnCl_6^{2+}$ molecule is 92.50 Å. The crystal system is **monoclinic** , and the space group is **$P2_1/c$** .

Information of plane spacing for monoclinic structure crystal systems.

$$\frac{1}{d^2} = \frac{1}{sin^2\beta} \cdot \left(\frac{h^2}{a^2} + \frac{k^2\, sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right)$$

V is the volume of the unit cell, given by $V=abc\sqrt[2]{1-\cos^2\beta}$.

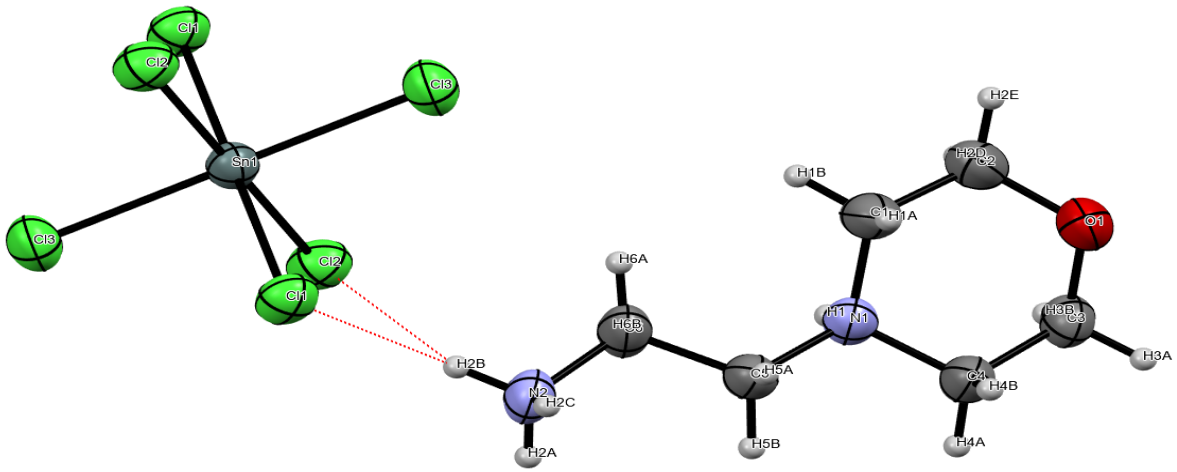


Fig-1. *(a) ORTEP drawing of the intermolecular H-bonds and (b) Nonlinear optical (NLO) materials.*

4-(2-ammonioethyl)morpholin-4-ium hexachlorostannate(IV).

molecule. Thermal ellipsoids are drawn with the 50% probability level.

Additionally, corrections for Lorentz and polarization effects were made to ensure the accuracy of the intensity measurements of the reflections.Monoclinic , Axial lengths and angles -Three unequal axes, one pair not at right angles $a \neq b \neq c$, $\alpha \neq \gamma = 90 \neq \beta$.

The X-ray diffraction data for the crystal structure of 2-Methyl-4-nitrobenzenaminium hexachloro-stannane monohydrate was collected using a KUMA Diffraction KM-4 four-circle single-crystal diffractometer.(Fig-1).

The crystal structure analysis was performed using a CCD detector with Mo Kα radiation (λ = 0.71073 Å). Data were processed using the CrysAlis program, applying an absorption correction. The structure of 4-(2-ammonioethyl)morpholin-4-ium hexachlorostannate(IV) was solved by direct methods and refined using the full-matrix least-squares method with SHELXL-97. Crystallographic data 4-(2-ammonioethyl)morpholin-4-ium hexachlorostannate(IV) (CCDC-905995) are available at www.ccdc.cam.ac.uk or from the Cambridge Crystallographic Data Centre. Further details are provided in Table 1.

Table 1. Crystallographic data and details of the refinement of the 4-(2-ammonioethyl)morpholin-4-ium hexachlorostannate(IV) structure.

Identification code	New complex
Empirical formula	$C_{12}H_{32}Cl_8N_4O_2Sn$
Formula weight	666.70
Temperature/K	293(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	9.2611(7)
b/Å	11.9762(4)
c/Å	12.3153(6)
α/°	90
β/°	110.616(6)
γ/°	90
Volume/Å^3	1278.45(13)
Z	2
ρ_{calc}g/cm^3	1.732
μ/mm^{-1}	15.788
F(000)	668.0
Crystal size/mm^3	0.2 × 0.18 × 0.16
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.206 to 152.164

Index ranges	$-11 \le h \le 11, -14 \le k \le 14, -10 \le l \le 15$
Reflections collected	8799
Independent reflections	2637 [R_{int} = 0.0854, R_{sigma} = 0.0700]
Data/restraints/parameters	2637/0/127
Goodness-of-fit on F^2	1.115
Final R indexes [I>=2σ (I)]	R_1 = 0.0579, wR_2 = 0.1617
Final R indexes [all data]	R_1 = 0.0810, wR_2 = 0.1958
Largest diff. peak/hole / e Å^{-3}	0.15/-0.18

Table-2.Bond Lengths for 4-(2-ammonioethyl)morpholin-4-ium hexachlorostannate(IV).

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Sn1	Cl1^1	2.4293(16)		N1	C4	1.491(9)
Sn1	Cl1	2.4293(16)		O1	C3	1.405(10)
Sn1	Cl2^1	2.438(2)		O1	C2	1.415(10)
Sn1	Cl2	2.438(2)		N2	C6	1.484(9)
Sn1	Cl3	2.4160(19)		C1	C2	1.517(11)
Sn1	Cl3^1	2.4160(19)		C5	C6	1.532(10)
N1	C1	1.494(10)		C4	C3	1.517(10)
N1	C5	1.491(9)				

Table-3.Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for

for 4-(2-ammonioethyl)morpholin-4-ium hexachlorostannate(IV).

Atom	*x*	*y*	*z*	U(eq)
H1	5450.07	6886.32	4419.04	52
H2A	9055.58	8118.29	7110.45	58
H2B	9062.49	7302.07	7985.59	58
H2C	8062.51	8273.84	7786.27	58
H1A	3302.23	7247.89	5523.67	64
H1B	4325.07	6174.32	5665.8	64
H5A	5618.67	8409.4	6188.9	54
H5B	6696.32	8492.34	5453.61	54
H4A	4787.93	8619.08	3577.53	60
H4B	3584.71	8786.47	4200.09	60
H3A	2310.21	8171.58	2287.08	56
H3B	3359.58	7104.32	2528.73	56
H6A	6687.12	6677.29	6943.25	60
H6B	7669.08	6658.73	6129	60

H2D	3036.9	5696.52	3727.4	67
H2E	1815.67	5846.05	4334.78	67

The percent elemental composition of compound 1 was determined using a Thermo Scientific FlashSmart (CHNS/O) elemental analyzer. This analysis was performed by gas chromatographic separation of combustion gases based on the modified Dumas method.

In order to assess the accuracy of the measurements, the results obtained from the analysis were compared in practical and theoretical terms.

Compound	Mr	compared	C %	H %	N %	O %	Cl %	Sn %
1.	666.73 26gr/mole	Theoretical	21.62	4.84	8.4	4.79	42.54	17.8
		Practical	21.57	4.805	8.375	4.74	45.51	17.75

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