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NONLINEAR OPTICAL (NLO) MATERIALS: BIS(2-METHYL-4-NITROANILINIUM) HEXACHLORO-TIN(IV) MONOHYDRATE.SINGLE CRYSTAL X-RAY STRUCTURE ANALYSIS

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Abstrakt.
2-Methyl-4-nitroaniline (2m4na) and Tin(IV) chloride formed a nonlinear optical material. The molecula obtained nonlinear optical material (NLO)=$(2m4na)_2SnCl_6 \cdot H_2O$-bis(2-Methyl-4-nitroanilinium) hexachloro-Tin (IV) monohydrate**.** 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.

Introduction

The design and synthesis of new organic-inorganic hybrid compounds have become significantly important in recent years due to the potential to merge the distinct properties of organic and inorganic materials. The self-assembly processes of these hybrid compounds in the solid-state are facilitated by a diverse array of interactions, including hydrogen bonding networks, π-π interactions, and van der Waals forces.These interactions play a crucial role in governing the supramolecular organization and properties of the resulting materials. The hydrogen bonding

network contributes to the structural stability and organization of the hybrid compounds. π-π interactions, which involve the stacking of aromatic systems, can influence the electronic properties and structural arrangement of the materials. Additionally, van der Waals forces contribute to the overall cohesion and packing efficiency of the hybrid structures.

Keywords: 2-Methyl-4-nitroaniline ; Single crystal; Hydrogen bond; Hirshfeld surface analysis; Crystal Voids.

Results and discussion.

1.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 N1-H•••Cl3 and N1-H•••Cl2 occurs between Cl2 and between N1-H•••H-O hydrogen bonds. The intermolecular bond is N1-H•••Cl2 distance is 2.579 Å and distance of N1-H•••Cl2 is 2.883 Å. The valence angle of Cl-Sn-Cl in the $SnCl_6^{2+}$ molecule is 92.50 Å.

Information of plane spacing for monoclinic structure crystal systems.

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

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≠b≠c, α≠γ=90≠β.

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).

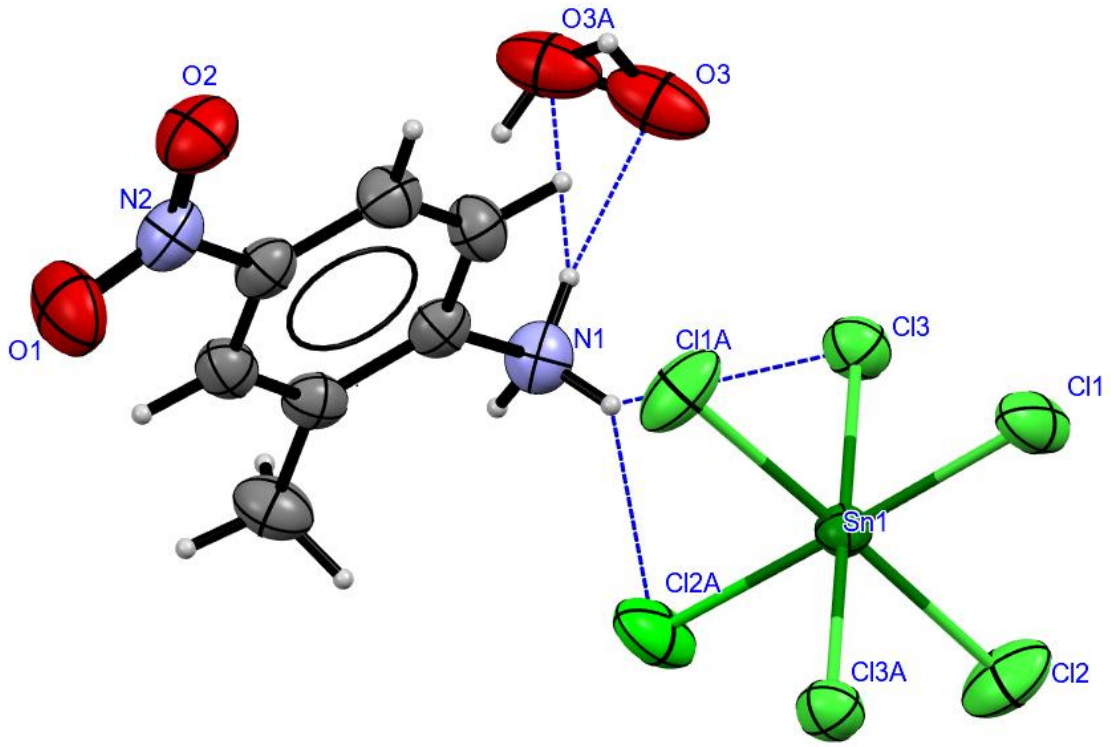

Fig-1. (a) ORTEP drawing of the intermolecular H-bonds and (b) Nonlinear optical (NLO) materials.

bis(2-Methyl-4-nitroanilinium) hexachloro-Tin(IV) monohydrate molecule. Thermal ellipsoids are drawn with the 50% probability level.

This instrument was equipped with a CCD detector and utilized graphite-monochromatized Mo Kα radiation with a wavelength of 0.71073 Å.

The raw data obtained from the diffraction experiment were processed using the CrysAlis Data Reduction Program, specifically version . During the data reduction process, an absorption correction was applied to account for any absorption effects present in the crystal sample.

The crystal structures of 2-Methyl-4-nitrobenzenaminium hexachloro-stannane monohydrate were initially solved using direct methods. Subsequently, the structures were refined utilizing the full-matrix least-squares method with the SHELXL-97 software. This refinement process allowed for a detailed and precise

analysis of the crystal structure, ensuring that the final model accurately represented the arrangement of atoms within the compound.

The crystallographic data for 2-methyl-4-nitroanilinium chloride (1) can be accessed through CCDC-875783 and for bis(2-amino-4-nitroanilinium) hexachloridostannate(IV) monohydrate (2) through CCDC-905995. Supplementary data related to the crystallography in this study can be acquired at no cost from www.ccdc.cam.ac.uk/conts/retrieving.html or by contacting the Cambridge Crystallographic Data Centre at 12 Union Road, Cambridge CB21EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.uk.

Crystallographic data and details of the structure refinement are given in Table 1.

Table 1. Crystallographic data and details of the refinement of the bis(2-Methyl-4-nitroanilinium) hexachloro-tin(IV) monohydrate. structure.

Name	**bis(2-Methyl-4-nitroanilinium) hexachloro-tin(IV) monohydrate.**
Empirical formula	**$2(C_7H_9N_2O_2^+)Cl_6Sn^{2+}\ H_2O$**
Formula weight	**655.71**
Temperature/K	**295(2)**
Crystal system	**Monoclinic**
Space group	**C2/c**
a/Å	**12.5392(3)**
b/Å	**9.2956(2)**
c/Å	**20.6018(4)**
α/°	**90**
β/°	**99.435(2)**
γ/°	**90**

V/Å^3	**2368.85**
Z	**1**
ρ_{calc}, g/cm^3	**1.342**
μ/mm^{-1}	**0.895**
F(000)	**848.0**
Crystal size/mm^3	**0.16 × 0.14 × 0.12**
Radiation	**Cu Kα (λ = 1.54184)**
2Θ range for data collection/°	**8.13 to 152.25**
Index ranges	**100 ≤ h ≤ -100, 100 ≤ k ≤ -100, 100 ≤ l ≤ -100**
Reflections collected	**13000**
Independent reflections	**2045 [R_{int} = 0.0297, R_{sigma} = 0.0159]**
Data/restraints/parameters	**2045/0/180**
Goodness-of-fit on F^2	**1.055**
Final R indexes [I>=2σ (I)]	**R_1 = 0.0343, wR_2 = 0.0940**
Final R indexes [all data]	**R_1 = 0.0372, wR_2 = 0.0969**
Largest diff. peak/hole / e Å^{-3}	**0.20/-0.15**
R-Factor(%)	**2.06**
Reduced Cell Parameters	**a: 7.804 b: 7.804 c: 20.602**

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