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Weak hydrogen bonds in bis(3-nitroanilinium) hexachloridostannate monohydrate. X-ray, vibrational and theoretical studies



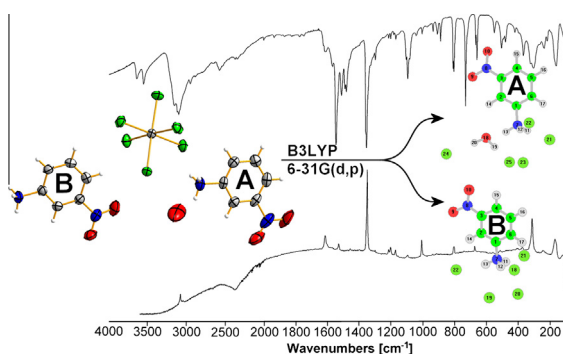
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HIGHLIGHTS

- Crystal structure of $(\text{H3NA})_2\text{SnCl}_6 \cdot \text{H}_2\text{O}$ was determined.
- Potential energy surface showed very low barrier upon rotation of the NH_3^+ group.
- Hydrogen bonds were included in theoretical calculations of the spectra.
- Calculations were carried out for the $[(\text{A-H3NA})\text{Cl}_5 \cdot \text{H}_2\text{O}]^{4-}$ and $[(\text{B-H3NA})\text{Cl}_5]^{4-}$ anions.
- Elementary graph-set descriptors were used to describe hydrogen bonding patterns.

GRAPHICAL ABSTRACT



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ABSTRACT

Crystal structures of bis(3-nitroanilinium) hexachloridostannate monohydrate, $(\text{H3NA})_2\text{SnCl}_6 \cdot \text{H}_2\text{O}$, was determined by means of X-ray single crystal diffraction. Relaxed potential energy surface of the H3NA^+ ion was calculated at the B3LYP/6-31(d,p) level. The energy of the H3NA^+ ion is approximately independent upon rotation of the ammonio group. It significantly depends on relative position of the nitro group towards aromatic ring. Theoretical spectra were calculated for the $[(\text{A-H3NA})\text{Cl}_5 \cdot \text{H}_2\text{O}]^{4-}$ and $[(\text{B-H3NA})\text{Cl}_5]^{4-}$ anions, and thus hydrogen bonds of the ammonio group with the nearest neighboring atoms were included. PED results revealed that no coupling among all of the N–H oscillators exists. They vibrate separately because each hydrogen atom of the ammonio group of A- and B- H3NA^+ ions has different surroundings of the acceptors. Overall, very good agreement between theoretical and experimental frequencies was achieved.

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Introduction

Influence of the amino and nitro groups on the non-linear properties of compounds was observed many years ago during extensive investigations on the nitroaniline derivatives [1,2]. Among the nitroanilines, 3-nitroaniline (3NA) crystallizes in non-centrosymmetric $Pca2_1$ space group [3–6] and thus optically active [1,2]. The 3NA can coordinate metal ions due to lone pair on the

nitrogen atom of the amino group. However, literature data on the coordination chemistry of the 3NA are very scarce. In the *Cambridge Structural Database*, the only three crystal structures are deposited [7–9]. Similarly, four crystal structures of protonated form, H3NA^+ , are known *i.e.* sulfate, perchlorate and two polymorphs of chloride salt [4,10–12].

In this work, the crystals of bis(3-nitroanilinium) hexachloridostannate monohydrate $(\text{H3NA})_2\text{SnCl}_6 \cdot \text{H}_2\text{O}$ were obtained. Recent studies showed that N–H...Cl hydrogen bonds are weaker in the hexachloridostannates than in simple chlorides [13]. In such molecular systems, internal vibrations of the H3NA^+ ion are

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expected to be weakly influenced by hydrogen bonds and therefore experimental spectra can be easily interpreted with the help of theoretical spectra. In spite of weakness of the hydrogen bonds in $(\text{H3NA})_2\text{SnCl}_6 \cdot \text{H}_2\text{O}$, theoretical spectra were calculated for the in-crystal geometry of two symmetry independent H3NA^+ ions with the nearest neighboring atoms of the NH_3^+ group. Besides, the assignment of the experimental bands are facilitated because the frequencies of the organic and inorganic part of the hybrid compound are well separated from each other.

Experimental

Synthesis

The starting compounds, 3-nitroaniline [Aldrich, purum, $\geq 98\%$ (NT)], hydrochloric acid (Aldrich, 40 wt% in H_2O , 99.95%) and tin(II) chloride (POCh Gliwice, 99.95%) were used as supplied. The SnCl_2 (2.23 mmol, 0.7805 g) and 3NA (4.45 mmol, 0.6147 g) were dissolved in 5 ml HCl and 20 ml methanol, respectively. Afterwards, the solutions were mixed together and slowly evaporated at room temperature for several days until the formation of single crystals of bis(3-nitroanilinium) hexachloridostannate monohydrate.

Single crystal X-ray diffraction studies

X-ray diffraction data were collected on a KUMA Diffraction KM-4 four-circle single crystal diffractometer equipped with a CCD detector using graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The raw data were treated with the CrysAlis Data Reduction Program (version 1.172.32.6) taking into account an absorption correction. The intensities of the reflection were corrected for Lorentz and polarization effects. The crystal structures were solved by direct methods [14] and refined by full-matrix least-squares method using SHELXL-97 program [14] (Table 1). Non-hydrogen atoms were refined using anisotropic displacement parameters. H-atoms were visible on the Fourier difference maps, but placed by geometry and allowed to refine “riding on” the parent atom with the exception of hydrogen atoms of the water molecule because of large anisotropic displacement parameters of the oxygen atom.

Table 1
Crystal data and structure refinement for the $(\text{H3NA})_2\text{SnCl}_6 \cdot \text{H}_2\text{O}$.

Chemical formula	$(\text{C}_6\text{H}_7\text{N}_2\text{O}_2)_2\text{SnCl}_6 \cdot \text{H}_2\text{O}$
M_r	627.68
Crystal system, space group	Triclinic, $P-1$
a, b, c (Å)	7.1380(3), 12.1472(5), 13.5776(6)
α, β, γ (°)	111.732(4), 93.919(4), 90.213(4)
V (Å ³)	1090.50(8)
Z , Calculated density	2, 1.912
m (mm ⁻¹)	1.94
Crystal size (mm)	0.42 × 0.26 × 0.07
Θ range for data collection	2.84–27.48
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14534, 4915, 3563
Completeness to θ	98.1%, 27.48 deg
$T_{\text{min}}, T_{\text{max}}$	0.325, 0.548
R_{int}	0.042
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.031, 0.074, 1.00
Data/restraints/parameters	4915/0/253
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.63, -0.61

Spectroscopic measurements

Room temperature FT-IR spectra in the 4000–400 cm^{-1} range were measured on the Bruker IFS-88 spectrometer with 2 cm^{-1} resolution. Nujol and fluorolube mull technique have been used in the measurements. Far-infrared spectra in the 550–50 cm^{-1} region were measured in Nujol suspension between polyethylene plates with 2 cm^{-1} resolution. Room temperature FT-Raman spectra were measured in the 3600–80 cm^{-1} range using Bruker FRA-106 attachment with 2 cm^{-1} resolution.

Computational details

All the computations were performed using density-functional theory (DFT) and hybrid Becke's three-parameter the Lee-Yang-Parr correlation functionals (B3LYP) [15–19]. The 6-31G(d,p) basis set was used, because it gives satisfactory results for vibrational data with respect to the computational costs [20]. The relaxed potential energy surface was calculated changing HNCC and ONCC dihedral angles which are connected to the rotation of the ammonio and nitro groups around C–N bonds. The surface was scanned in 0–120 deg range of rotation of the NH_3^+ group for dih(ONCC) = (0, 10, 20, 30, 60 and 90 deg) of the NO_2 group. At each and every point, the geometry parameters were optimized and a stationary point was reached with “tight” option for the singlet electronic ground state.

Frequencies of normal modes were calculated for the $[(\text{A-H3NA})\text{Cl}_5 \cdot \text{H}_2\text{O}]^{4+}$ and $[(\text{B-H3NA})\text{Cl}_5]^{4-}$ anions because two symmetry independent H3NA^+ ions exist in the unit cell and the ammonio groups are involved in $\text{N-H} \cdots \text{O/Cl}$ hydrogen bonds. The geometry of both anions were optimized with “tight” option. The position of all the atoms were taken from crystallographic data. Due to keeping the $[(\text{H3NA})\text{-5Cl} \cdot (\text{H}_2\text{O})]$ molecular arrangement preserved from the crystal structure, the positions of the chloride anions and water molecule in relation to the N_{NH_3} atom were constrained and not optimized. The same concerns dihedral angles of both the ammonio and nitro groups i.e. dih(H1A1–N1A–C1A–C2A) = 0.74 deg and dih(O1A–N2A–C3A–C2A) = 1.62 deg for A- H3NA^+ ion, and dih(H1B1–N1B–C1B–C2B) = 0.24 deg and dih(O1B–N2B–C3B–C2B) = 11.33 deg for B- H3NA^+ ion (Fig. 1a). Besides, these constraints were indispensable to avoid escape of the chloride anions to infinity during optimization.

Frequencies were scaled using scaling equation $\nu_{\text{sc}} = 0.9543 \cdot \nu_{\text{calc}} + 22.1$ introduced for benzene [20]. PED calculations were carried out using VEDA program [21–23]. The definitions of local modes are deposited as Supporting information.

Results and discussion

Crystal structure of bis(3-nitroanilinium) hexachloridostannate monohydrate

The $(\text{H3NA})_2\text{SnCl}_6 \cdot \text{H}_2\text{O}$ compound crystallizes in centrosymmetric space group $P-1$ with two H3NA^+ ions (A and B) in the asymmetric part of the unit cell (Fig. 1a). Contrary to the other hexachloridostannate salts where the anion lies on the inversion center [24–29] or on the twofold axis [13,30–32], the SnCl_6^{2-} anion lies in general position in the title compound. The water molecule lies in the channel formed along the b axis and is weakly hydrogen bonded by the ammonio group of organic cation (Fig. 1b).

Geometry data of interactions between the NH_3^+ group and SnCl_6^{2-} anion are collected in Table 2 and they are well visible on the Hirshfeld surface [33,34] (Fig. 2a). According to the Etter's notation of hydrogen bonding patterns [35] and elementary graph-set descriptors [36], the NH_3^+ group and the SnCl_6^{2-} anion

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