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The layered crystal structure of bis(theophyllinium) hexachloridostannate (IV), $C_{14}H_{18}N_8O_8SnCl_6$

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Abstract

$C_{14}H_{18}N_8O_8SnCl_6$, monoclinic, $P2_1/n$ (no. 14), $a = 8.1810(2)$ Å, $b = 12.6195(3)$ Å, $c = 11.3811(2)$ Å, $\beta = 90.258(2)^\circ$, $Z = 2$, $V = 1174.97(5)$ Å³, $R_{gt}(F) = 0.0266$, $wR_{ref} = 0.0620$, $T = 290$ K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.30 × 0.16 × 0.10 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.81 mm ^{−1}
Diffractometer, scan mode:	Xcalibur EOS, ω
θ_{max} , completeness:	33.0°, 98%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	17679, 4333, 0.025
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 3278
$N(param)_{refined}$:	165
Programs:	Diamond [1], CrysAlis ^{PRO} [2], SHELX [3, 4], ShelXle [5]

Source of material

All chemicals were obtained from commercial sources and used as purchased. The Raman spectra were measured using a Bruker MULTIRAM spectrometer (Nd: YAG-laser at 1064 nm; InGaAs detector) with an apodized resolution of 8 cm^{−1} in the region of 4000–70 cm^{−1}. The title compound was synthesized by dissolving 0.18 g (1 mmol) theophylline 180.16 and 0.14 SnCl₄ (0.5 mmol) in 1 mL concentrated hydrochloric acid. Short-time warming until both components were dissolved yielded a colourless solution. From the aforementioned colourless solution a large number of colourless block crystals grew upon slow cooling to room temperature within minutes.

Experimental details

A single crystal of the title compound was directly selected from the mother liquor and rapidly transferred to the Xcalibur four-circle diffractometer equipped with an EOS detector [2]. An absorption correction (Gaussian method) was applied [2]. The structure solution and the refinement were successfully carried out using the SHELX program system [3–5]. The pseudo-orthogonal unit cell (see the Figure and the Abstract) and the occupancy of special positions by the SnCl₆^{2−} anions causes a couple of minor difficulties during the semi-automated data collection

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
Sn1	0.500000	0.500000	0.500000	0.02128 (5)
Cl1	0.43257 (7)	0.48605 (6)	0.70878 (5)	0.04115 (14)
Cl2	0.51798 (9)	0.30903 (4)	0.48832 (6)	0.04624 (17)
Cl3	0.21278 (6)	0.49002 (5)	0.44895 (5)	0.03561 (12)
O1	0.52203 (19)	0.04847 (13)	0.64313 (15)	0.0351 (4)
O2	0.63937 (19)	0.31667 (13)	0.90004 (14)	0.0324 (3)
N1	0.5731 (2)	0.19005 (14)	0.76250 (16)	0.0268 (3)
N2	0.7595 (2)	0.13645 (13)	0.61508 (15)	0.0259 (3)
N3	0.9486 (2)	0.35070 (15)	0.75585 (16)	0.0276 (4)
H3	0.953 (3)	0.405 (2)	0.800 (2)	0.037 (7)*
N4	1.0039 (2)	0.24896 (15)	0.60733 (17)	0.0296 (4)
H4	1.052 (4)	0.227 (2)	0.542 (3)	0.054 (9)*
C1	0.6133 (3)	0.12098 (16)	0.67220 (19)	0.0265 (4)
C2	0.8569 (2)	0.21706 (16)	0.65178 (18)	0.0251 (4)
C3	0.8203 (2)	0.28065 (16)	0.74453 (17)	0.0243 (4)
C4	0.6753 (2)	0.26708 (16)	0.81081 (18)	0.0251 (4)
C5	1.0552 (3)	0.33142 (18)	0.6724 (2)	0.0316 (4)
H5	1.151389	0.369097	0.660252	0.043 (7)*
C6	0.4111 (3)	0.1765 (2)	0.8148 (2)	0.0389 (5)
H6A	0.367669	0.244483	0.835927	0.064 (6)*
H6B	0.419974	0.132962	0.883729	0.064 (6)*
H6C	0.339429	0.143028	0.758983	0.064 (6)*
C7	0.7991 (3)	0.0684 (2)	0.5151 (2)	0.0408 (6)
H7A	0.707185	0.065270	0.462509	0.100 (8)*
H7B	0.824267	−0.001657	0.542783	0.100 (8)*
H7C	0.891865	0.096789	0.474470	0.100 (8)*

strategy calculation. But an extended exposure time provides a reasonable I/σ ratio for the systematically weak reflections ($R(\sigma) = 0.0259$; $R(\sigma) = \Sigma [\sigma(F_o^2)]/\Sigma [F_o^2]$) and guarantees a plausible chemical model [6, 7]. In this case the resolution limit was set to 0.65 Å yielding a reflections/parameter ratio of 26.3/1. All hydrogen atoms were seen in the Fourier map after all non-hydrogen atoms were located. C-bound hydrogen atoms were included using a riding model. Coordinates of nitrogen-bound hydrogen atoms were refined using distance restraints and individually refined U_{iso} parameters. The maximum residual peak of 0.81 eÅ^{−3} and the deepest hole of −0.71 eÅ^{−3} are found 0.66 and 0.70 Å, respectively, from atom Cl2.

Comment

Introduction

Theophylline is a well-known natural product and was first described by Kossel in 1888 [8, 9]. He was able to isolate theophylline from tea leaves, which origins the naming up

to now. There is still a fundamental interest in this compound and the corresponding solid state phases [10, 11] and co-crystals [12–15]. Nowadays theophylline is often used as pharmaceutical agent due to its effects on the respiratory system [16–19]. Recently, theophylline was also used in SARS–CoV-2 therapy [20].

We have already shown that heterocyclic cations like some pyridinium derivatives [21, 22] and the derived *N*-protonated cations of naturally occurring bases like nicotine [23, 24], caffeine [25] and theophylline [26, 27] are excellent tectons to construct hydrogen bonded networks. A database check (Cambridge Structural database [28]) showed that not more than about 20 crystal structures have been deposited so far, that contain a theophyllinium cation. The SnCl₆^{2−} counterion used for this study is a bulky, medium-strong hydrogen-bond acceptor, which is sometimes used by us [29] and many other groups [30–36]. It should be mentioned that anionic Sn(IV) complexes are of current interest with mixed ligands that contain chlorido ligands and for example C₂F₅ [37] groups or benzyl groups [38], respectively. This contribution is part of our long-standing interest in the structures and hydrogen-bonding schemes of hexahalogenidometallates [6, 39].

From the reaction of theophylline (systematic name: 1,3-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione) with hydrochloric in the presence of one equivalent of SnCl₄, colorless block crystals of the title compound were obtained.

Structural comments

The asymmetric unit of the title compound consists of one *N*-protonated theophyllinium cation (TheoH) residing on a general position, and one half of a hexachloridostannate(IV) anion located on an inversion center. Bond lengths within the TheoH cation are all in the expected ranges [26, 27]. The same is true for the [SnCl₆]^{2−} anion [29–36]. In detail, the Sn–Cl distances range from 2.4182(5)–2.4482(6) Å and the *cis*-angles range from 89.63(2)–90.37(2)°. Each theophyllinium cation is connected to four neighbouring cations by classical NH...O hydrogen bonds (see the Figure). These connections construct a layered, hydrogen bonded structure in the (101) plane. In detail, the N–H donor groups of TheoH are involved in unbifurcated classical hydrogen bond (see the Figure; N3...O1' = 2.758(2) Å; ' = 1.5 − *x*, 0.5 + *y*, 1.5 − *z*; N4...O2'' = 2.739(2) Å; '' = 0.5 + *x*, 0.5 − *y*, −0.5 − *z*). Each mesh of the hydrogen-bonded net consists of four cations. It is obvious that larger and smaller meshes are present in this structure (see the Figure). Consequently, the [SnCl₆]^{2−} anions (Wyckoff site: 2a) are located beneath and above of the larger meshes, whereas two inversion symmetry related

methyl groups of two TheoH cations fill the smaller meshes around the Wyckoff sites $2b$ and $2c$.

The $[SnCl_6]^{2-}$ anion as a weak to medium-strong hydrogen-bond acceptor is not involved in any strong hydrogen bonds in the title structure. This was bound to happen as all classic hydrogen donors in the title structure are involved in medium-strong unbifurcated $NH\cdots O$ hydrogen bonds. Nevertheless the chlorido ligand Cl_2 , which features the shortest $Sn-Cl$ distance shows the longest $Cl\cdots H$ distance, which is in total accord with our expectations of a bulky anion interacting with neighbours via weak intermolecular forces. Thus we suppose that the shape and the group radius of the $[SnCl_6]^{2-}$ determines or at least supports the formation of the hydrogen-bonded, two-dimensional network.

This suggestion is supported by the fact that in the case of another theophyllinium salt (I_{10}^{2-} ; [26]) a related hydrogen bonded 2D network is obtained, which features only one type of a mesh formed by six theophyllinium cations. Also in the case of the $(TheoH)_2I_{10}$, the cyclic I_{10}^{2-} anions excellently fits with the shape of the hydrogen-bonded network formed by the TheoH cations.

Raman spectroscopy

There are three very strong signals in the Raman spectrum at 312, 162, and 135 cm^{-1} respectively as well as one medium-strong signal at 239 cm^{-1} . These four signals must be assigned to the $SnCl_6^{2-}$ anion and are similar to those for detected for $(PCL_4)_2SnCl_6$ [40] and K_2SnCl_6 [41].

Conclusion and outlook

We have shown that the counter anion may influence the hydrogen-bonding scheme of the theophyllinium sub system. Also typical for this class of compounds is the pseudosymmetric arrangement [42–45] of the anionic sub structure of the hexachloridostannate(IV) anions [39, 46]. We expect that further theophyllinium hexahalogenidometallate salts will be accessible using other metal-chlorides as educts: $M = Ir$ [39], Pb [46], Os [30], Pt [30].

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