

Three isomers in a (hydrogen L-Cysteinato)-thallium(I): Crystal structure, spectroscopic and thermal properties

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ABSTRACT

The isolation of thallium(I) complexes $[\text{Ti}_2(\text{HCys})_2]_n$ (**1**) and $[\text{Ti}_4(\text{HCys})_4]_n$ (**2**) ($\text{H}_2\text{Cys} = \text{L-Cysteine}$) from aqueous solution by means of crystallization is reported herein. Polar crystals of **1** and **2** were crystallized in $P2_1$ and $P2_12_12_1$ space groups respectively. Elemental analysis, XRD, IR, UV-Vis, TG-DSC and a single crystal X-ray diffraction were applied for characterizing the compounds. Linkage isomers **1** and **2** have 1D and 2D coordination polymeric structures respectively. The lone pair electrons of thallium(I) in **1-2** are stereo-chemically active. In **1**, each of two independent Tl^+ ions is coordinated by three HCys^- ions forming TiS_3O irregular polyhedron that is linked to each other by vertexes in an infinite chain. In **2**, four independent Tl^+ ions are coordinated by HCys^- ions through S and O atoms, forming TiS_3O_2 , TiS_4 , TiS_3S , TiS_3S_2 irregular polyhedrons. The crystallographic independent HCys^- ions are linked to the metal ion differently, two are $\mu_3\text{-S,S,S-}$, one is $\mu_4\text{-O,S,S,S-}$, and one is $\mu_4\text{-O,O',S,S,S-}$ coordinated ligands. The amine group of compounds **1** and **2** is in the form of an ammonium ion ($-\text{NH}_3^+$). The structures of **1-2** are stabilized by $\text{N-H}\cdots\text{O}$ hydrogen bonds, thalophilic $\text{Tl}\cdots\text{Tl}$ and anagostic $\text{Tl}\cdots\text{H-C}$ interactions. The spectroscopic and thermal properties of compounds were analyzed.

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1. Introduction

Compared to transition metals, very little attention is paid to thiolate coordination polymers of metal ions with a low valence p-block (Tl, Sn, and Pb) [1–3], although they can find application in chemistry of materials and medical technology due to their important optical and conductive properties [1,4]. These metal ions include a stereo-chemically active $6s^2$ lone pair with greater relativistic effects that may induce forming the coordination polymers with a unique structure. The coordination polymers of Tl(I) are least studied among them, in part because of their toxicity [5].

L-Cysteine (H_2Cys) is an important component of many enzymes [6]. It can also be considered as a model for protein and non-protein SH-bearing molecules [7]. Sulfhydryl, amine and carboxylate groups of H_2Cys have a coordination capacity for the Tl

(I) ion, which can be used to produce coordination polymers with a diverse structure. The NH_2 group in H_2Cys facilitates the generation of hydrogen bonds, which together with $\text{Tl}\cdots\text{Tl}$ thalophilic [8,9] and $\text{Tl}\cdots\text{H-C}$ interactions [10] can lead to the formation of unique supramolecular ensembles.

In this work, we report on the crystallization of three hydrogen isomers of L-cysteino-thallium(I) from aqueous medium. The fundamental aims of the present study are to trace the changes of the solid-state structure and the coordination mode of HCys in $[\text{Ti}(\text{HCys})]_n$ depending on crystallization conditions (pH, thallium salt and reagents concentration). Herein, the structure of two novel coordination polymers $[\text{Ti}(\text{HCys})]_n$ is solved by the X-ray single crystal technique. All isomers were also characterized by elemental analysis, TG-DSC, FT-IR and UV-Vis spectra.

2. Reagents and synthesis

L-Cysteine [CAS 52-90-4] was commercially available from Sigma-Aldrich. Thallium(I) nitrate, thallium(I) chloride, NaOH and HNO_3 were obtained as a reagent analytical grade (Merck) and they were used without additional purification.

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2.1. Synthesis of crystal 1

0.077 g (0.64 mmol) of L-H₂Cys was added to 2 ml of a 0.32 M solution of TlNO₃, containing 0.64 mmol of thallium, and then the pH of the solution was adjusted to 9 with 0.1 M NaOH solution. By this time, the solution had become yellow. Within an hour, a precipitate was formed consisting mainly of yellow crystals and a small number of orange crystals. The solution with crystals was left at 5–6 °C for 1 day. When stored in a refrigerator, orange crystals dissolve, and the amount of yellow crystals increases. The yellow crystals in the form of sticks were filtered, dried between sheets of filter paper and kept in the air at room temperature to constant weight. The yield was 86%. A single crystal for the X-ray diffraction analysis was selected directly from the total mass of the product.

Anal. Calc. for C₆H₁₂N₂O₄S₂Tl₂ (**1**): C, 11.1; H, 1.86; N, 4.32; S, 9.88. Found: C, 11.2; H, 1.69; N, 4.22; S, 10.2%.

2.2. Synthesis of crystal 2

0.1 g (0.42 mmol) of solid TlCl was added to 0.102 g (0.84 mmol) of L-H₂Cys in 5 ml of water. The pH of the mixture was adjusted to 7 with 0.1 M NaOH solution. The resulting mixture was left for a day at room temperature. The orange crystals and a small number of rectangular yellow-orange crystals of **2** were filtered and washed with acetone; then yellow-orange crystals were mechanically selected for further analysis. The yield was 10–20%.

Anal. Calc. for C₁₂H₂₄N₄O₈S₄Tl₄ (**2**): C, 10.1; H, 1.86; N, 4.32; S, 9.88. Found: C, 10.8; H, 1.99; N, 4.19; S, 9.99%.

2.3. Synthesis of crystal 3

0.102 g (0.84 mmol) of L-H₂Cys and 5 ml of water were added to 0.1 g (4.2 mmol) of solid TlCl and the pH was adjusted to 9 with the solution of 0.1 M NaOH. The resulting oil-like yellow phase, while stirring the mixture, initially changed its color to yellow-orange, and then the orange crystalline powder in the form of thin plates slowly precipitated. After one day, it was filtered, washed with acetone and dried in the air at room temperature to the constant weight. The yield was 95–97%. We have not managed to obtain crystals suitable for single-crystal X-ray diffraction structural characterization.

Anal. Calc. for C₃H₆NO₂STl (**3**): C, 11.1; H, 1.86; N, 4.32; S, 9.88. Found: C, 11.4; H, 1.84; N, 4.24; S, 10.1%.

Minor changes in the synthesis conditions of **1–3** (pH, the ratio of reagents, thallium salt) led to the formation of a crystal mixture. During the contact of the precipitate with the mother liquor, phase transformations were often observed, accompanied by a change in the shape and color of the crystals. As a rule, the main product of these transformations was phase **1**. Complexes **1–3** were insoluble in water, acetone, acetonitrile, and ethanol, but more soluble in DMSO, probably due to their polymeric nature.

3. X-ray diffraction analysis

The intensity patterns were collected from single crystals **1** and **2** at 296 K using the SMART APEX II single crystal diffractometer (Bruker AXS, analytical equipment of Krasnoyarsk Center of Instruments Shared Use of SB RAS) equipped with a CCD-detector, graphite monochromator and Mo K α radiation source. The absorption corrections were applied using the SADABS program. The structures were solved by the direct methods using package SHELXS and refined in the anisotropic approach for non-hydrogen atoms using the SHELXL program [11]. All hydrogen atoms were found via Fourier difference maps. Further the hydrogen atoms linked with C, N atoms in the (**1**) and (**2**) were positioned geomet-

rically as riding on their parent atoms with $d(\text{C-H}) = 0.93\text{--}0.98 \text{ \AA}$, $d(\text{N-H}) = 0.89 \text{ \AA}$ depending on the geometry and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$. The structure test for the presence of missing symmetry elements and possible voids was made using the PLATON software [12]. The DIAMOND software was used for the crystal structure plotting [13].

Powder X-ray diffraction data of **1–3** were obtained using the D8 ADVANCE diffractometer (Bruker, analytical equipment of Krasnoyarsk Center of collective use of SB RAS) equipped by a VANTEC detector with an Ni filter. The measurements were made using Cu K α radiation. The structural parameters defined by a single crystal analysis of **1–2** were used as basic in powder pattern Rietveld refinement. The refinement was produced using TOPAS 4.2 software [14]. Low *R*-factors and good refinement results shown in (Fig. 1S) indicate the crystal structures of the powder samples to be a representative of the bulk structures.

The unit cell parameters of **3** were determined using TOPAS 4.2 software. Only two possible space groups can be chosen, *P*-1 and *P*1, but namely *P*1 should be chosen because the compound contains an ion of optical active molecule – L-Cysteine. Profile fitting of experimental pattern by this unit cell was stable and gave low *R*-factors (Table 1S, Fig. 2S).

4. Physical measurements

IR absorption spectra of the compounds were recorded over the range of 400–4000 cm⁻¹ at room temperature on a VECTOR 22 Fourier spectrometer (SFU CEJU). The chemical analysis was carried out with an HCNS-0 EA 1112 Flash Elemental Analyser (Perkin-Elmer, England). TGA was carried out on a simultaneous SDT-Q600 thermal analyzer (TA Instruments, USA, SFU CEJU) under dynamic air atmosphere (50 ml/min flow rate) within 25–480 °C at the scan rate of 10 °C/min. The compound weight was 8.947 mg for **1**, 3.719 mg for **2** and 6.133 for **3**. Platinum crucibles with perforated lids were used as containers. UV-Vis spectra were recorded on an Evolution 300 spectrophotometer (Thermo Scientific, UK) using 1 cm quartz cells.

5. Results and discussion

5.1. Crystal structures of 1

The unit cell of [Tl₂(HCys)₂]_{*n*} (**1**) corresponds to monoclinic symmetry. A space group *P*2₁ was determined from the statistical analysis of the reflection intensities and extinction rules. The main crystal data are shown in Table 1. The main bond lengths defined are shown in Table 2. The Tl–S [2.882(6)–3.213(6) Å] and Tl–O [2.842(6), 2.971(6) Å] distances fall near the values found in Tl(DL-HCys) [15] and other related compounds [16,17]. The bond distances and angles of the L-HCys⁻ ligands are comparable to those found in other cysteinate complexes. Similar to Tl(DL-HCys), the ligand dimensions in **1–2** do not differ significantly from those of the free H₂Cys [18]. The mean S–C bond length is 1.84 Å, the mean C–C bond length is 1.53 Å (Table 2). Sulfur atom of the HCys⁻ is tetrahedrally surrounded by three thallium atoms and one carbon atom.

The asymmetric unit of **1** comprises two Tl⁺ ions and two HCys⁻ ions (Fig. 1a). Each Tl⁺ ion is coordinated by three HCys⁻ ions through three S and one O atoms, forming TlS₃O irregular polyhedron. The presence of the lone pair 6s² generally results in a non-spherical charge distribution around metal cations in solids, and furthermore, leads to lowering the coordination symmetry of the ligands around them, so called being stereo-chemically active. The fact that all the identifiable bonds lie on one side of the Tl atom indicates that the lone-pair electrons are stereo-chemically active.

Table 1
Crystal structure parameters of (1) and (2).

Single crystal	Tl ₂ (HCys) ₂ (1)	Tl ₄ (HCys) ₄ (2)
Moiety formula	C ₆ H ₁₂ N ₂ O ₄ S ₂ Tl ₂	C ₁₂ H ₂₄ N ₄ O ₈ S ₄ Tl ₄
Dimension (mm)	0.3 × 0.25 × 0.1	0.2 × 0.2 × 0.1
Color	yellow	yellow
Molecular weight	649.04	1298.07
T (K)	296	296
Space group, Z	P2 ₁ , 2	C2, 4
a (Å)	10.0088 (7)	24.575 (2)
b (Å)	4.8561 (3)	10.3792 (6)
c (Å)	13.2134 (9)	9.5955 (6)
α (°)	90	90
β (°)	108.417 (2)	92.092 (2)
γ (°)	90	90
V (Å ³)	609.33 (7)	2445.8 (3)
ρ _{calc} (g/cm ³)	3.538	3.525
μ (mm ⁻¹)	26.754	26.661
Reflections measured	12 679	15 199
Reflections independent	5865	6024
Reflections with F > 4σ(F)	2638	5367
2θ _{max} (°)	73.01	56.41
h, k, l – limits	−16 ≤ h ≤ 16; −8 ≤ k ≤ 8; −22 ≤ l ≤ 21	−32 ≤ h ≤ 32; −13 ≤ k ≤ 13; −12 ≤ l ≤ 12
R _{int}	0.1184	0.0708
The weighed refinement of F ²	w = 1/[σ ² (F _o ²) + (0.0004P) ²], P = (F _o ² + 2F _c ²)/3	w = 1/[σ ² (F _o ²)]
Number of refinement parameters	146	290
R1 [F _o > 4σ(F _o)]	0.0628	0.0405
wR2	0.0988	0.0745
Goof	0.982	0.973
Δρ _{max} (e/Å ³)	3.27	1.31
Δρ _{min} (e/Å ³)	−2.37	−1.51
(Δ/σ) _{max}	0.000	0.000

In contrast to **1**, a Tl⁺ ion with five neighbors was found in a (hydrogen DL-Cysteinato)-thallium(I) [15], in which Tl(I) is bound with three sulfur and two oxygen atoms. In **1**, the HCys[−] ion acts as a bidentate (O, S) and bridging ligand, which is additionally linked to two other thallium atoms through a sulfur atom. Taking into account the coordination mode of the ligand, the short formula has the form of [Tl₂(HCys–O,S,S,S)₂]_n. The polyhedrons in **1** are

linked to each other by vertexes and form an infinite chain along b-axis (Fig. 2). There are several 6- and 8-membered rings involving Tl, O and S atoms (Figs. 3a, 3Sa).

The metal–metal distances of d(Tl1...Tl1) 3.66 Å and d(Tl2...Tl2) 3.56 Å (Table 2) are shorter than the sum of the van der Waals radii (4.00 Å) [18] indicating significant thalophilic interactions (Figs. 2, 3a). The crystallographic asymmetric unit of **1** with these bonds is shown in Fig. 4Sa. Then the polyhedron of Tl1 atom is a distorted octahedra and the polyhedron Tl2 is a distorted square prism. As a result of the thalophilic interaction, the three Tl1 atoms are linked together in a chain just like the three Tl2 atoms (Fig. 3a). The angles ∠Tl1–Tl1–Tl1 and ∠Tl2–Tl2–Tl2 are 83.02(3) and 86.01(4)° respectively. If we take into consideration that all the distances Tl...Tl are less than 4.20 Å, then two alternative zigzag infinite chains along the b-axis consisting of Tl1 or Tl2 atoms are formed (Fig. 2). The closest Tl1...Tl2 contact of 4.5497 (15) Å between these zigzag chains shows a lack of metalphilic interaction. Of course, the cation–cation interactions are weaker than most covalent or ionic bonds but stronger than other van der Waals bonds, and roughly comparable with typical hydrogen bonds in strength.

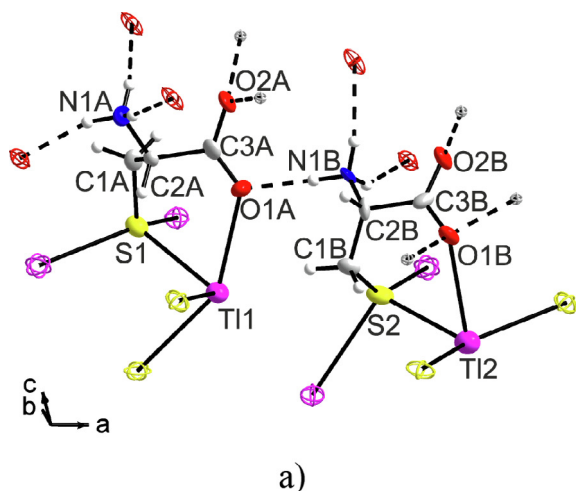
Recently, considerable efforts have been focused on the less common bonding interactions involving the metals (M) and a C–H bond on the ligand fragments in complexes due to their possible implications in organic synthesis via activation of C–H bond and supramolecular synthons. M...H–C interaction is divided into the agostic and anagostic. The agostic bond is a true 3-centre-2-electron bond (a d(M...H) ≈ 1.8–2.3 Å), and the anagostic bond is largely of electrostatic interaction [10]. The reports on the existence of C–H...Tl interactions are rare [20–22], and therefore subject to intense investigation. The Tl atoms in **1** are linked to the methylene hydrogen atoms of the HCys[−]. The distances Tl...H are in the range of 3.16–3.48 Å, which corresponds to the formation of weak anagostic bonds. In other metal–organic complexes of Tl(I) the Tl...H–C distances lie in the range of 3.06–3.34 Å [20]. It is to be noted that Tl...H–C distances observed in these complexes are longer than values found in previous work with d⁸ metal ions [22] in the range of 2.61–2.89 Å, but this can be attributed to the larger size of the Tl(I) ion.

Table 2
Main geometric parameters (Å, °) of **1** and **2**.

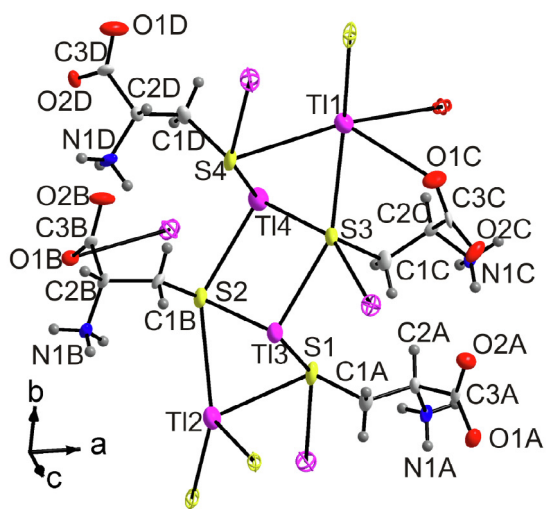
[Tl ₂ (HCys) ₂] _n (1)					
Tl1–S1	2.969 (6)	S1–C1A	1.83 (2)	S2–C1B	1.84 (2)
Tl1–S2 ⁱ	3.042 (6)	O1A–C3A	1.23 (2)	O1B–C3B	1.26 (2)
Tl1–S1 ⁱⁱ	3.131 (6)	O2A–C3A	1.26 (2)	O2B–C3B	1.24 (2)
Tl1–O1A	2.842 (6)	N1A–C2A	1.47 (2)	N1B–C2B	1.47 (2)
Tl2–S2	2.882 (6)	C1A–C2A	1.53 (3)	C1B–C2B	1.52 (3)
Tl2–S1 ⁱⁱⁱ	3.164 (5)	C2A–C3A	1.55 (2)	C2B–C3B	1.51 (3)
Tl2–S2 ⁱⁱ	3.213 (6)	Tl1–Tl1	3.6637 (12)	Tl2–Tl2	3.5599 (14)
Tl2–O1B	2.971 (6)	Tl1–Tl2	4.5497 (15)	Tl1–Tl2	5.6506 (14)
[Tl ₄ (HCys) ₄] _n (2)					
Tl1–S3	3.072 (4)	S1–C1A	1.815 (13)	S2–C1B	1.836 (13)
Tl1–O1C	3.110 (4)	O1A–C3A	1.249 (15)	O1B–C3B	1.264 (15)
Tl1–O1B ⁱ	3.217 (4)	O2A–C3A	1.247 (14)	O2B–C3B	1.228 (15)
Tl1–S4	3.268 (4)	N1A–C2A	1.486 (16)	N1B–C2B	1.480 (16)
Tl1–S1	3.268 (4)	C1A–C2A	1.511 (17)	C1B–C2B	1.527 (17)
Tl2–S1	3.005 (4)	C2A–C3A	1.532 (16)	C2B–C3B	1.541 (16)
Tl2–S3 ⁱⁱ	3.117 (4)	Tl1–Tl4	3.6790 (8)	Tl2–Tl3	3.4534 (8)
Tl2–S4	3.247 (4)	Tl1–Tl4	3.7103 (9)	Tl3–Tl4	4.1122 (8)
Tl2–S2	3.251 (4)	Tl1–Tl2	4.001 (8)	Tl3–Tl4	4.001 (8)
Tl3–S1	2.918 (4)	S3–C1C	1.803 (13)	S4–C1D	1.827 (13)
Tl3–S2	2.921 (3)	O1C–C3C	1.231 (15)	O1D–C3D	1.245 (16)
Tl3–S3	3.010 (3)	O2C–C3C	1.260 (15)	O2D–C3D	1.264 (15)
Tl4–S4	2.819 (4)	N1C–C2C	1.503 (14)	N1D–C2D	1.462 (16)
Tl4–S3	3.017 (4)	C1C–C2C	1.527 (18)	C1D–C2D	1.528 (17)
Tl4–S2	3.082 (4)	C2C–C3C	1.522 (16)	C2D–C3D	1.523 (16)

Symmetry codes for:

Tl₂(HCys)₂ (1): (i) −x + 1, y + 1/2, −z; (ii) x, y − 1, z; (iii) −x + 1, y − 1/2, −z.Tl₄(HCys)₄ (2): (i) −x + 1/2, y + 1/2, −z; (ii) −x + 1/2, y − 1/2, −z + 1.



a)



b)

Fig. 1. The asymmetric unit of the $[Ti_2(HCys)_2]_n$ (a), $[Ti_4(HCys)_4]_n$ (b) unit cell. All atoms in the asymmetric unit are labeled. The neighboring symmetry-generated atoms are represented by principal ellipses with an individual color. The intermolecular hydrogen bonds in **1** are represented by dashed lines, the H-bonds in **2** were not showed for simplicity and figure clarity. The ellipsoids are drawn at the 50% probability level, except for the hydrogen atoms represented by spheres. (Color online.)

There are six intermolecular hydrogen bonds N–H...O in the structure (Fig. 3b, Table 2S) which form a 3D network. This is a 4-nodal net with stoichiometry $(3-c)(4-c)(8-c)(9-c)$ and with a vertex symbol $(3.4^7.5^{12}.6^7.7)(3^2.4^3.5)(3^6.4^9.5^{12}.6^7.7^2)(4^3)$ which is known as 3,4,8,9T1 in ToposPro database [23]. Only on MANGEP compound in the CSD database has the same net of hydrogen bonds, but it has no chemical similarities with the compound under investigation. There are supramolecular motifs $R_2^2(10)$ and $R_4^4(12)$ can be marked in **1**.

5.2. Crystal structures of **2**

The unit cell of $[Ti_4(HCys)_4]_n$ (**2**) corresponds to monoclinic symmetry. The statistical analysis of the reflection intensities and extinction rules allowed to determine a space group C2. The main crystal data are shown in Table 1. The main bond lengths defined

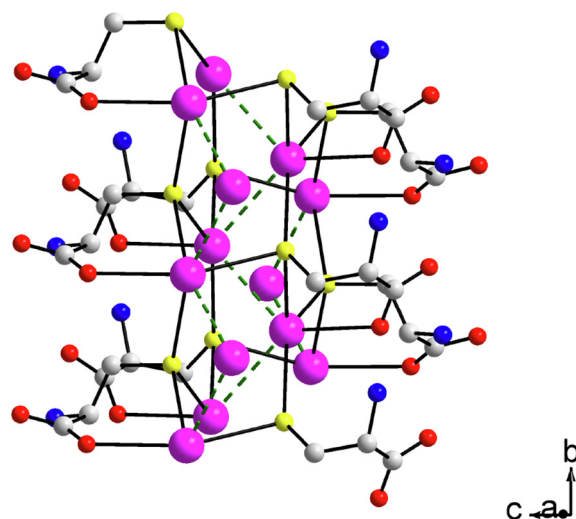
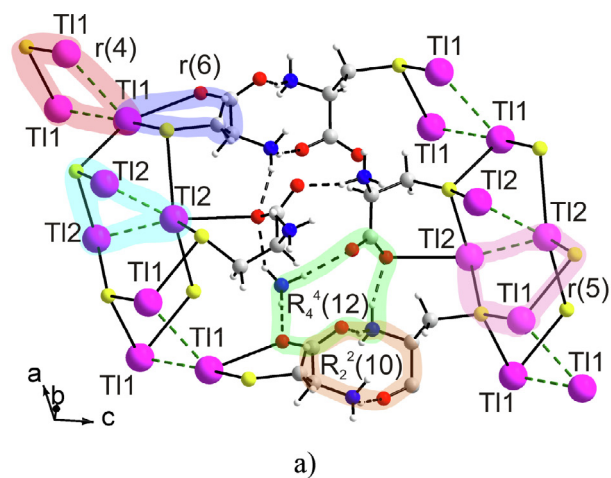
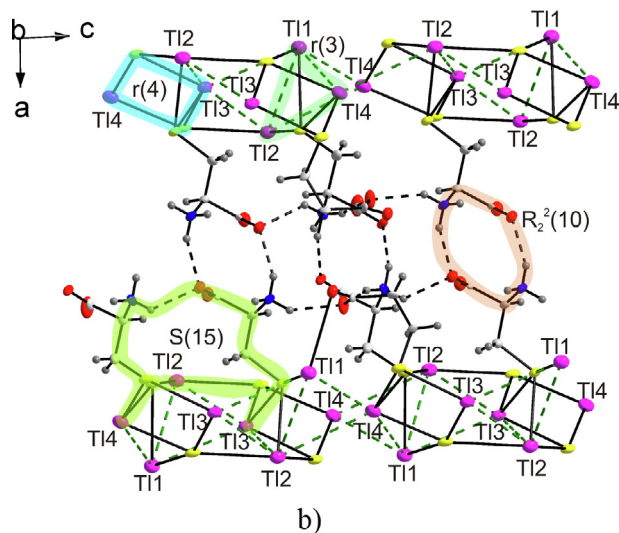


Fig. 2. The column of TiS_3O polyhedra along b -axis in **1**. The $Ti \cdots Ti$ interactions are marked by dashed lines.



a)



b)

Fig. 3. Hydrogen bonding and $Ti \cdots Ti$ interactions in **1** (a) and **2** (b). The H-bonds are marked by dashed lines, the H-bond motifs are marked by circles.

are shown in Table 2. The $Ti-S$ distances [2.819(4)–3.268 (4) Å] fall near the values found in other related compounds [16,17]. $Ti-O$ bond lengths of 3.110(4) and 3.217 (4) Å are longer than

those for Tl(DL-HCys) [15] (2.86 and 3.06 Å), however similar and even larger distances Tl–O are established in other structures [16] for example 3.21 and 3.40 Å in [24]. The bond distances and angles of the hydrogen L-Cysteinato ligand are comparable to those found in Tl(DL-HCys) [15] and free H₂Cys [18]. The mean S–C bond length is 1.82 Å, the mean C–C bond length is 1.52 Å, for details see Table 2. The sulfur atoms of the L-HCys[−] could be divided into two groups: S1, S2 and S4 have a tetrahedral environment and are bonded to three thallium atoms and one carbon atom, and S3 has a tetragonal environment of four thallium atoms and one carbon atom.

The asymmetric unit contains four Tl⁺ ions and four HCys[−] ions (Fig. 1b). The Tl1⁺, Tl2⁺, Tl3⁺ and Tl4⁺ ions are coordinated by four, four, three and three L-HCys[−] ions, respectively, through S and O atoms, forming Tl1S₃O₂, Tl2S₄, Tl3S₃, Tl4S₃ irregular polyhedrons. These polyhedrons are linked with each other by edges of two S atoms with the formation of a four-membered ring r(4), containing two Tl and two S atoms, and 2D layer in *bc*-plane (Fig. 5S). As in 1 (Fig. 2a), there is an eight-membered ring containing alternating Tl and S atoms (Fig. 3Sb).

In contrast to **1**, in this complex, the ligand environment of crystallographic independent thallium atoms and the coordination modes of independent HCys[−] ions (A, B, C, D) are different. The HCys[−] (C) ion is bound bidentately through the O and S atoms with the Tl1 atom and with three metal atoms (Tl2, Tl3, Tl4) through the bridging atom S3. This is the first complex of the HCys[−] ion, where the sulfur atom is simultaneously bound to four metal atoms [17]. In one structurally characterized Ag(I) complex [25] (code in CSD MIQWIV), the S atom of the doubly charged Cys^{2−} anion is also bound to four metal atoms. The HCys[−] (A and D) ions are μ₃-S,S,S-coordinated ligands, and the HCys[−] (B) ion is μ₄-O,S,S,S-coordinated ligand.

Coordination polymers **1–2**, having the same chemical formula {Tl(HCys)}_n but different structure are isomers. The Tl(I) ions in them have different values of the coordination number, and the ligands have different coordination modes that allow to attribute **1–2** to linkage isomers. Linkage isomerism is the existence of coordination compounds that have the same composition differing in the connectivity of the metal to a ligand [25]. It occurs with ambidentate ligands that are capable of coordinating in more than one way. Linkage isomers have different physical and chemical properties [26,27]. The structural complexity and the lack of single crystals prevented full structural characterization of compound **3**, even in the presence of an indexed powder diffraction pattern (Fig. 2S, Table 1S).

The shortest Tl⋯Tl distances within the chains lie in the range of 3.45–4.11 Å (Table 2), which indicates thalophilic interactions. If we take into consideration these short contacts, then each independent thallium atom is connected to the other three (Fig. 3b, 4Sb) with the formation of a three-dimensional network. The values of ∠Tl1–Tl1–Tl1 and ∠Tl2–Tl2–Tl2 are 83.02(3) and 86.01(4)° respectively. Taking the intermetallic interactions Tl⋯Tl into account, the coordination number for Tl1 and Tl2 is 8, and for Tl3 and Tl4 is 6. The coordination geometry of these polyhedrons is irregular, that is, the lone electron pair is stereo-chemically active.

All Tl atoms in **2** are bonded to the hydrogen atoms of methylene groups. Thallium atoms are involved in the interaction of Tl⋯H–C with both coordinated HCys[−] ions (intramolecular interaction) and those are not directly connected to them (intermolecular interaction). Tl⋯H distances are in the range of 2.86–3.28 Å and these contacts can be considered as weak anagostic bonds [19].

There are 12 intermolecular hydrogen bonds N–H⋯O in the structure (Fig. 2b, Table 2S) which form a 3D network. This is a 8-nodal net with stoichiometry (4-c)(4-c)(4-c)(5-c)(8-c)(9-c)(10-c)(10-c) and with vertex symbol (3².4¹⁰.5¹².6³.7)(3².4³.5)(3².4⁴)₂

(3².4⁶.5²)(3⁴.4¹².5¹⁶.6³.7)(3⁴.4¹³.5²⁰.6⁷.7)(3⁶.4¹⁵.5¹⁹.6⁵) which is new in ToposPro database [23]. There are two supramolecular motifs S(15) and R₂²(10) can be marked in **2**.

5.3. The pH effect on the formation of thallium(I) cysteinates

L-Cysteine (⁺NH₃–CH(CH₂SH)–COO[−]) exists in its anionic forms (HCys[−] and Cys^{2−}), zwitterion species (H₂Cys), and cationic form (H₃Cys⁺). The logarithms of Cys^{2−} protonation constants at 25 °C and ionic strength 0.5(NaClO₄) in aqueous solution are 1.48 ± 0.04, 8.02 ± 0.09, and 9.92 ± 0.11 for carboxylic, sulfhydryl, and amino groups respectively [28]. The formation of neutral Tl (HCys), anionic Tl(Cys)[−] [28–30] and cationic Tl(H₂Cys)⁺ [30] species was established in aqueous solution, and their stability constants were determined.

$$\begin{aligned}\beta_{121} &= [\text{Tl}(\text{H}_2\text{Cys})^+]/\{[\text{Tl}^+]\cdot[\text{H}^+]^2\cdot[\text{Cys}^{2-}], \\ \beta_{111} &= [\text{Tl}(\text{HCys})]/\{[\text{Tl}^+]\cdot[\text{H}^+]\cdot[\text{Cys}^{2-}], \\ \beta_{101} &= [\text{Tl}(\text{Cys})^-] / \{[\text{Tl}^+]\cdot[\text{Cys}^{2-}]\}.\end{aligned}$$

The values of logβ₁₁₁ = 11.29 in 0.15 M NaCl medium at 37 °C [28] and logβ₁₁₁ = 11.0 at ion strength 0.1 M (NaClO₄) and 25 °C [30] were obtained by potentiometric titrations using a glass electrode. Taking into account the differences in the ionic medium, temperature, and also experimental errors, the obtained values of β₁₁₁ do not contradict each other. The logβ₁₀₁ values differ more significantly: 3.27 [29], 11.6 [28] and 3.95 [30]. In the range of pH 2–4, the formation of the cationic Tl(H₂Cys)⁺ complex (logβ₁₂₁ = 2.47) was also suggested, and at pH 3 its mole fraction is about 40% [30]. According to [30], in the range of pH 5–7, the mole fraction of Tl(HCys) in aqueous solution reaches almost 100%, but other data show that it does not exceed 10% [29]. The presence of a neutral complex with the general formula of Tl(HCys) in the pH range 5–9 is indirectly confirmed by the results of our study and it is consistent with the literature data [28–30]. Isomer **2** is formed at pH 7, and isomers **1** and **3** are precipitated at pH 9. The formation of two different isomers at the same pH value can be attributed to the difference in their crystallization conditions (pH and thallium salt).

5.4. Coordination modes of the HCys[−] ion in the metal complexes

In most of its complexes, cysteine acts as a tridentate ligand, through N, S and O atoms, e.g. in Ni[Mo₂O₂S₂(Cys)₂·14H₂O [31], or less common bidentate, through O and S, e.g. in [Bi(Bipy)(H₂O)(HCys–O,S) [32], and through N and S in [Pd₆(HCys)₁₀](NO₃)₂·11-H₂O [33]. Relatively few complexes were structurally characterized, in which HCys[−] acts as a unidentate ligand, for example, as in Bi(HCys–S)₃ [34]. In structurally characterized complexes, simultaneous binding of HCys[−] ions only through the N and O atoms was not detected, and coordination through the N atom is always preceded by coordination through the S atom. In part, this can be explained by the lower acidity of –NH₃⁺ group compared to the –SH group [28]. A single-crystal X-ray diffraction analysis shows that **1** and **2** have the same formula, but different structure. In the [Tl₂(HCys–O,S,S,S)₂]_n complex, HCys[−] ion acts as a bidentate (O, S) and a bridging (S,S) ligand, and in [Tl₄(HCys)₄]_n (**2**) independent ligands adopt different coordination modes (μ₃-S,S,S, μ₄-O,S,S, S and μ₄-O,S,S,S). The formation of coordination polymers in the solid state suggests their existence in relatively concentrated aqueous solutions along with mononuclear species [28–30].

5.5. Spectroscopic study

The IR spectra of **1–3** are significantly different from the spectra of starting materials and this indicates the formation of new

compounds. All assignments for peaks in the spectrum of L-Cysteine are given in [35]. In the spectrum of L-Cysteine, taking the zwitterionic form, the peaks observed at 2522 and 692 cm^{-1} are assigned to $\nu(\text{SH})$ and $\nu(\text{C}=\text{S})$, respectively, they are absent in spectra of **1–3** (Fig. 6S). We therefore conclude that, in **1–3**, the sulfur in the sulfhydryl group of cysteine forms a sulfur–thallium bond. This is not surprising as the S atom is known to have binding ability to “soft” metal elements, thallium(I) in particular. The broad peaks at 3443 (**1**), 3462 (**2**), 3423 (**3**) cm^{-1} are attributed to NH_3^+ stretching. The peaks at 1052 (**1**), 1058 (**2**) and 1056 cm^{-1} (**3**) are attributed to NH_3^+ rocking, and the peaks at 1522 (**1**), 1484 (**2**), 1527 cm^{-1} (**3**) are assigned to NH_3^+ bending. Thus, the amine group of **1–3** is in the ammonium ion form ($-\text{NH}_3^+$), which is consistent with our SCXR study. In spectra of **1–3**, we attribute the strong peaks in the range of 1620–1567 cm^{-1} to $\nu(\text{CO})$ of COO^- group binding to a metal ion [35–37]. The IR spectra in all compounds are similar, which allows to assume that the HCys[−] ligands in them are linked to Tl(I) through S and O atoms.

The UV–Vis spectra of **1** in DMSO solutions exhibit the broad band centered at ca. 264 nm ($\epsilon = 4150$) (Fig. 7S). The spectra of compounds **2** and **3** contain less intense band at 314 nm ($\epsilon = 1640$) and 317 nm ($\epsilon = 1700$) respectively. All these bands are assigned to charge transfer $\text{HCys}^- \rightarrow \text{Ti}^+$. The UV–Vis spectra of **2** and **3** are very similar, i.e. they form the same complex species in DMSO. This anticipates that compound **3** has a polymeric structure similar to compound **2**. The electronic absorption spectrum of compound **1** in DMSO differs markedly from that considered above and does not contain a long-wavelength band. This indicates the formation of another species.

5.6. Thermal decomposition

The TG–DSC curves of **1–3** are shown in Figs. 8S–10S, respectively. The similarity of the TG–DSC curves in the range of 225–480 °C indicates the same sequence of decomposition stages under oxidative conditions (in the air). The stability of compounds **1–3** below 180–190 °C confirms their anhydrous character. The gradual weight loss of sample **3** when heated up to 180 °C is related to its hygroscopicity. The decrease in the mass of the substances in the range of 180–225 °C corresponds to the oxidation of compounds **1–3** with gases evolved. In this range, the mass of the samples decreased rapidly in accordance to the mean TG curves. The TG and DSC curves clearly indicate that thermal decomposition/oxidation of **1–3** occurs in several steps (Figs. 8S–10S).

An experimental weight loss (Δm) of 20.3% for **1**, 20.6% for **2**, and 20.1% for **3** at 225 °C best corresponds to the formation of Tl_2SO_4 ($\Delta m_{\text{theor}} = 22.2\%$), which is indirectly confirmed by the release of SO_2 at $T > 420$ °C. The first stage of decomposition is accompanied by endo effect at 201 °C for **1**, 209 °C for **2** and 190 °C for **3**. According to the IR spectroscopic analysis of the gases evolved, in the range of 180–225 °C CO_2 , H_2O and NH_3 are formed. In the second stage, the TG curves become more sloping and the mass loss reaches a minimum at ~ 290 °C. At this stage, predominantly SO_2 and COS are evolved. The total mass loss at 290 °C is 23% for **1**, 24% for **2** and **3** also most closely corresponds to the formation of Tl_2SO_4 ($\Delta m_{\text{theor}} = 22.2\%$). In the range of 290–420 °C for **1** and 290–380 °C for **2** and **3**, the mass of the samples increases due to the oxidation of Tl (I) to Tl (III), and with further increase in temperature, the mass of the samples decreases due to decomposition of oxidation products. The transformations of **1**, **2** and **3** at 225–450 °C are accompanied by the exo effects at 233, 297, 395 °C, 249, 312, 341 °C and 239, 292 °C, respectively. The similarity of the TG–DSC, UV–Vis and IR spectra of **1–3** shows that compound **3** also has a polymer structure.

6. Conclusions

Three crystalline Tl(HCys) isomers were obtained by the interaction of thallium salts with L-Cysteine in aqueous medium. Isomer **1** was crystallized at pH 9 and equimolar amounts of TlNO_3 and H_2Cys . Isomer **2** was prepared at a molar ratio of $\text{TlCl}:\text{H}_2\text{Cys} = 1:2$ and pH 7, and isomer **3** was obtained at a molar ratio of $\text{TlCl}:\text{H}_2\text{Cys} = 1:1$ and pH 9. Thus, the use of different thallium salts and pH values in the synthesis leads to the formation of three isomers. The coordination polymers **1–2** are linkage isomers. Although isomer **3** is not structurally characterized, it is most likely, that it also has a polymer structure. In **1**, the HCys^- ligands are bonded to the Tl(I) centers in chelating–bridging $\mu_3\text{-O}_3\text{S}_3\text{S}$ coordination mode. In **2**, independent HCys^- ions are linked with Tl(I) by diverse coordination modes ($\mu_3\text{-S}_3\text{S}$, $\mu_4\text{-O}_3\text{S}_3\text{S}$ and $\mu_4\text{-O}_3\text{S}_3\text{S}$). As a result, the coordination environment of independent thallium atoms and the coordination modes of independent ligands are different. HCys^- ions have preferred coordination through the sulfur atom which is in a good agreement with the HSAB principle. In **1–2**, the thallium atoms sit in irregular HCys^- environments suggesting that their lone electron pairs are stereo-chemically active. The closest Tl···Tl distances are 3.66 Å and 3.56 Å in **1**, and 3.45–4.11 Å in **2** indicating thalophilic interactions. There are intermolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds in the structures of **1–2** form the 3D networks. Tl···H–C anagostic interactions additionally stabilize the structure of compounds. IR spectra of **1–2** are consistent with the X-ray diffraction data. Anhydrous compounds **1–3** have the same sequence of thermal decomposition stages in the air. The data on the structure and properties of the three Tl(HCys) isomers obtained in this work expand our knowledge on the coordination polymers containing thiolate ligands.

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Appendix A. Supplementary data

CCDC 1920591 and 1920592 contains the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data to this article can be found online at <https://doi.org/10.1016/j.poly.2019.114141>.

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