


## Article

# A New Mineral Hanauerite, AgHgSI, and Common Crystal Chemical Features of Natural Mercury Sulphohalides

Igor V. Pekov <sup>1,\*</sup>, Natalia V. Zubkova <sup>1</sup>, Sergey N. Britvin <sup>2,3</sup> , Atali A. Agakhanov <sup>4</sup>, Yury S. Polekhovskiy <sup>2,†</sup>, Dmitry Y. Pushcharovskiy <sup>1</sup>, Gerhard Möhn <sup>5</sup>, Joy Desor <sup>6</sup> and Günter Blass <sup>7</sup>

<sup>1</sup> Faculty of Geology, Moscow State University, Vorobiev Gory, 119991 Moscow, Russia; n.v.zubkova@gmail.com (N.V.Z.); dmitp@geol.msu.ru (D.Y.P.)

<sup>2</sup> Institute of Earth Sciences, St. Petersburg State University, University Emb. 7/9, 199034 St. Petersburg, Russia; sbritvin@gmail.com

<sup>3</sup> Nanomaterials Research Center, Kola Science Center, Russian Academy of Sciences, 184209 Apatity, Russia

<sup>4</sup> Fersman Mineralogical Museum of the Russian Academy of Sciences, Leninsky Prospekt 18-2, 119071 Moscow, Russia; atali99@mail.ru

<sup>5</sup> Dr.-J.-Wittmannstrasse 5, 65527 Niedernhausen, Germany; gerhard.moehn@yahoo.de

<sup>6</sup> Im Langenfeld 4, 61350 Bad Homburg, Germany; joydesor@gmail.com

<sup>7</sup> Merzbachstrasse 6, D-52249 Eschweiler, Germany; nc-blaszgu@netcologne.de

\* Correspondence: igorpekov@mail.ru

† Deceased 28 September 2018.

**Abstract:** A new mineral, hanauerite, ideally AgHgSI, was found in the oxidation zone of Ag- and Hg-bearing ores at two old, abandoned mines in Rhineland-Palatinate, Germany. In a holotype specimen originating from the Schöne Aussicht Mine, Dernbach, Westerwald, it is associated with plumbogummite–hinsdalite series of minerals and goethite. In cotype from the Friedrichsseggen Mine, Bad Ems, it is associated with perroudite, goethite, and quartz. At both localities, hanauerite occurs as a prismatic crystal up to 0.15 mm long and up to 0.02 mm thick. The mineral is yellow, transparent, with an adamantine lustre. It is brittle, and cleavage was not observed. The calculated density values are 6.671 and 6.575 g cm<sup>-3</sup> for holotype and cotype, respectively. The empirical formulae calculated (from electron microprobe data) based on the sum of all atoms = 4 *apfu* are Ag<sub>0.95</sub>Hg<sub>1.00</sub>S<sub>1.01</sub>(I<sub>0.83</sub>Br<sub>0.19</sub>Cl<sub>0.03</sub>)<sub>Σ1.05</sub> for holotype and Ag<sub>0.97</sub>Hg<sub>0.97</sub>S<sub>1.05</sub>(I<sub>0.76</sub>Br<sub>0.25</sub>)<sub>Σ1.01</sub> for cotype. Hanauerite is orthorhombic, space group *Pmma*; the unit cell parameters (from single-crystal X-ray diffraction data; holotype/cotype) are: *a* = 9.932(2)/9.9256(8), *b* = 4.6219(19)/4.6209(2), *c* = 9.891(4)/9.9006(4) Å, *V* = 454.0(3)/454.19(5) Å<sup>3</sup>, and *Z* = 4. The crystal structure was studied on single crystals extracted from both holotype and cotype specimens; *R*<sub>1</sub> = 0.0416 (holotype) and = 0.0544 (cotype). In hanauerite, Hg<sup>2+</sup> cations centre strongly distorted octahedra with two short Hg–S bonds (Hg and S atoms build “crankshaft-type” chains) and four strongly elongated Hg–I bonds. The Hg-centred octahedra are connected via common edges and faces to form corrugated layers; Ag<sup>+</sup> cations are located between these layers. Hanauerite is named in honour of the German mineral collector Dr. Alfred Hanauer (1912–1988). The common crystal chemical features of mercury sulphohalide minerals are discussed.

**Keywords:** hanauerite; new mineral; silver mercury sulphide iodide; mercury sulphohalide; crystal structure; oxidation zone of ore deposit; Schöne Aussicht Mine; Friedrichsseggen Mine



**Citation:** Pekov, I.V.; Zubkova, N.V.; Britvin, S.N.; Agakhanov, A.A.; Polekhovskiy, Y.S.; Pushcharovskiy, D.Y.; Möhn, G.; Desor, J.; Blass, G. A New Mineral Hanauerite, AgHgSI, and Common Crystal Chemical Features of Natural Mercury Sulphohalides. *Crystals* **2023**, *13*, 1218. <https://doi.org/10.3390/cryst13081218>

Academic Editor: Carlos Rodriguez-Navarro

Received: 5 July 2023

Revised: 1 August 2023

Accepted: 3 August 2023

Published: 6 August 2023



**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

Natural mercury sulphohalides compose a specific—in terms of both geochemistry and crystal chemistry—family of minerals. They form in the oxidation zone of ore deposits containing primary Hg-bearing minerals, the most commonly found cinnabar- or/and Hg-enriched fahlore. Besides mercury, these minerals can effectively concentrate such scattered-in-nature elements as bromine and iodine. This family contains ten mineral

species and can be subdivided to two sub-families. One of them consists of six minerals with the general formula  $\text{Hg}_3\text{S}_2\text{Hal}_2$  (*Hal* = halogen: Cl, Br, I), namely three polymorphs of  $\text{Hg}_3\text{S}_2\text{Cl}_2$  (corderoite [1], lavrentievite [2,3], and kenhsuite [4]); dimorphous arzakite [2,3] and grechishchevite [5–7], with the ideal end-member formula  $\text{Hg}_3\text{S}_2\text{Br}_2$ ; and radtkeite  $\text{Hg}_3\text{S}_2\text{ICl}$  [8–10]. The second sub-family contains four sulphohalide minerals with both Hg and Ag as metal cations: dimorphs of  $\text{AgHgSCl}$  (capgaronnite [11] and iltisite [12]); perroudite,  $\text{Ag}_4\text{Hg}_5\text{S}_5(\text{I,Br})_2\text{Cl}_2$  [13–15]; and a recently discovered hanauerite,  $\text{AgHgSI}$ , first described in the present paper. Hanauerite is related to capgaronnite and iltisite in stoichiometry, their chemical analogue being species-defining I instead of Cl; however, these three Ag–Hg sulphohalides strongly differ from each other in symmetry, unit cell dimensions, and powder X-ray diffraction patterns that reflect the structure differences.

The type specimens of hanauerite were collected from two old, abandoned mines located in Rhineland-Palatinate, Germany. The holotype specimen, for which electron microprobe analyses (EMPA), optical data, single-crystal and powder X-ray diffraction (XRD) data were obtained and crystal structure was determined, originates from the Schöne Aussicht Mine, Dernbach, Neuwied, Wied Iron Spar District, Westerwald. The locality of the cotype specimen, for which EMPA and single-crystal XRD data were obtained and crystal structure was determined, is the Friedrichssegen Mine, Frücht, Bad Ems District, Lahn valley.

The new mineral is named in honour of the prominent German mineral collector Dr. Alfred Hanauer (1912–1988). He was a pioneer in the collecting of micromounts in Germany and Central Europe in the early 1960s. Dr. Hanauer collected at the Schöne Aussicht Mine the specimens in which the mineral described here was first found.

Both the new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA2018–045) [16]. The type specimens of hanauerite are deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, with the catalogue numbers 96264 (Schöne Aussicht Mine) and 96265 (Friedrichssegen Mine).

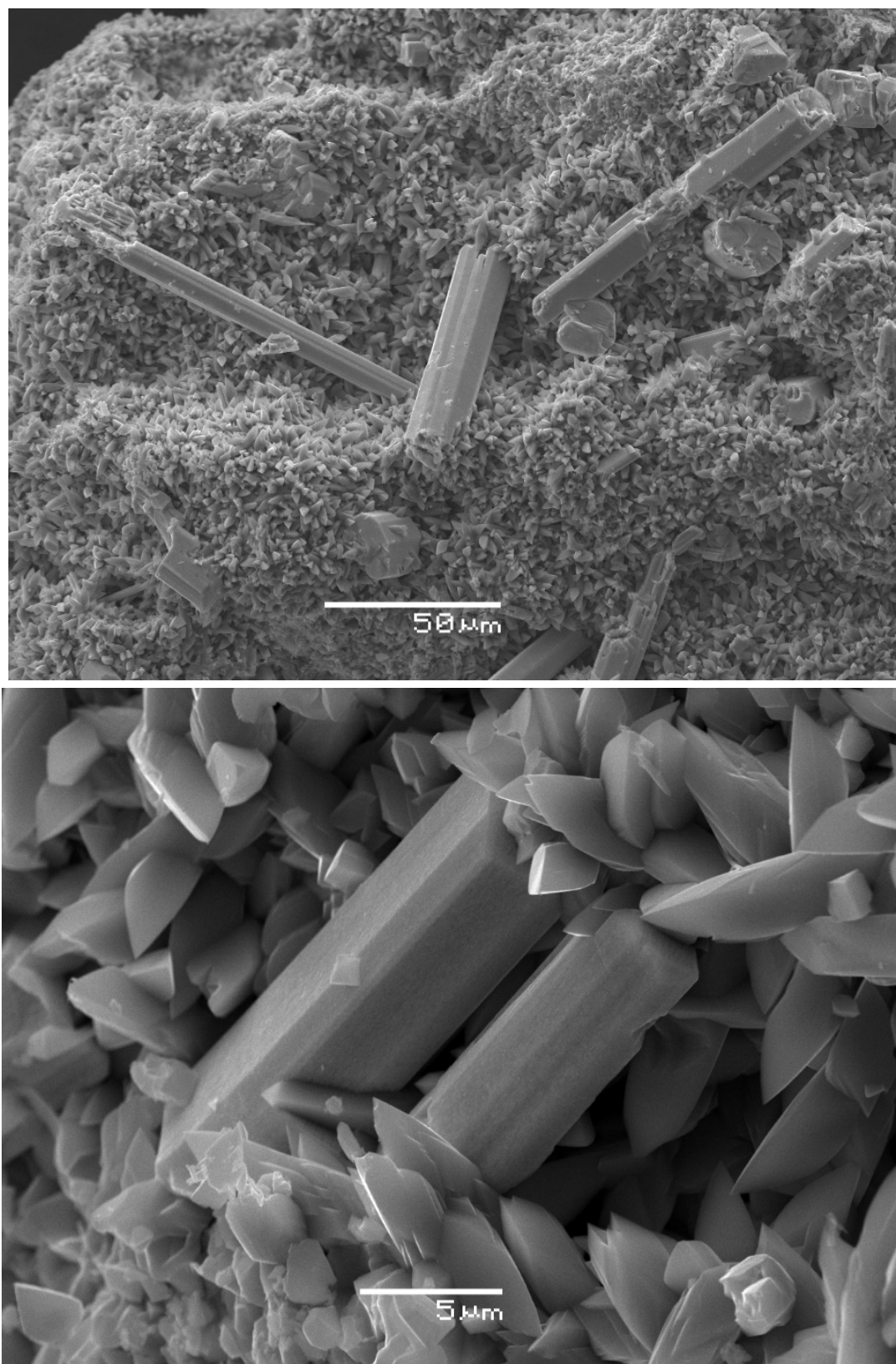
## 2. Materials and Methods

### 2.1. Occurrence, General Appearance, and Physical Properties

Hanauerite is a secondary, supergene mineral formed in the oxidation zone of the complex sulphide ores containing primary silver and mercury sulphide mineralization. At both localities, the new mineral occurs as isolated prismatic crystals, elongated along [010], up to 0.15 mm long and up to 0.02 mm thick in cavities of the oxidized ores. The crystal faces belonging to the  $\{h0l\}$  zone are major and the pinacoid {010} is the major form on terminations. At the Schöne Aussicht Mine, hanauerite is associated with plumbogummite–hinsdalite series minerals in cavities of goethite (limonite) aggregates (Figures 1 and 2). At the Friedrichssegen Mine, hanauerite occurs in association with perroudite, goethite, and quartz.

The general mineralogical data for the Schöne Aussicht Mine and the Friedrichssegen Mine are reported in [17] and [18], respectively.

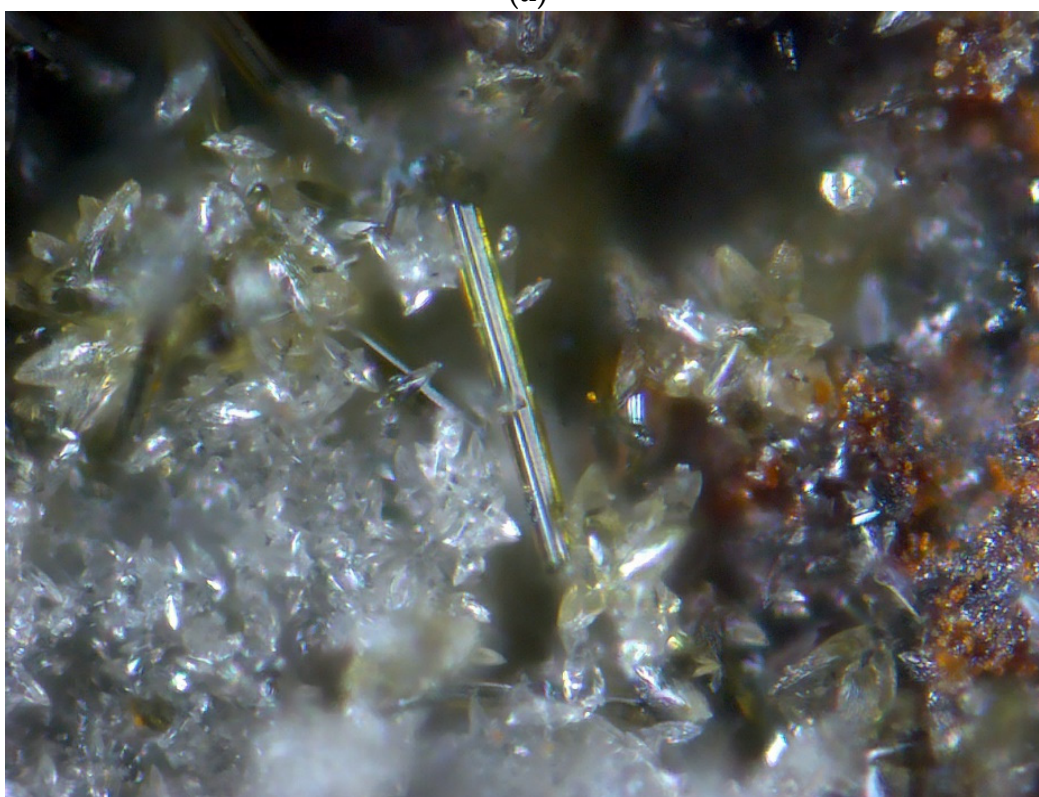
Fresh hanauerite from both localities is yellow; however, like some other silver or mercury halides, it is photosensitive and darkens after exposure to strong light (especially under sunlight), becoming almost black. Hanauerite has an adamantine lustre; fresh crystals are transparent, whereas altered under light crystals are semi-transparent to almost opaque. The mineral is brittle, cleavage or parting was not observed, the fracture is uneven. The density values calculated using the empirical formulae are 6.671 and 6.575 g cm<sup>−3</sup> for holotype and cotype, respectively. The difference is caused by different I:Br ratios (see below).



**Figure 1.** Prismatic crystals of hanauerite on crusts consisting of sharp rhombohedral plumbogummite crystals. Schöne Aussicht Mine. SEM (SE) images.



(a)



(b)

**Figure 2.** Yellow prismatic crystals of hanauerite on goethite and aggregates of greenish-yellow rhombohedral plumbogummite crystals. Schöne Aussicht Mine. FOV width: (a)—1.2 mm, (b)—0.35 mm.

## 2.2. Methods

**Optical studies.** The reflectance values for hanauerite were measured by means of the MSF-21 microspectrophotometer (LOMO, St. Petersburg, Russia) using the SiC standard (Zeiss, No. 545).

**EMPA.** For the determination of chemical composition, hanauerite crystals were embedded into epoxy resin, polished and coated with carbon film. Electron microprobe data were obtained by means of a JEOL Superprobe JXA-733 instrument. Quantitative analyses were performed in wavelength-dispersive mode under accelerating voltage of 20 kV, beam current 10 nA and beam diameter 5  $\mu\text{m}$ . The following standards were used:  $\text{Ag}_2\text{Te}$  (Ag),  $\text{HgTe}$  (Hg),  $\text{ZnS}$  (S), atacamite (Cl),  $\text{TlBr}$  (Br), and  $\text{CuI}$  (I). The contents of other elements with atomic numbers higher than carbon were below detection limits.

**Powder XRD** data were obtained using a Rigaku RAXIS Rapid II diffractometer (curved image plate, Debye-Scherrer geometry,  $r = 127.4$  mm,  $\text{CoK}\alpha$ , rotating anode with microfocus optics, 40 kV, 15 mA, exposure 15 min). Data conversion was performed by means of osc2xrd programme [19].

**Single-crystal XRD** studies were carried out using a Bruker Kappa APEX DUO diffractometer for the holotype specimen and using an Xcalibur S diffractometer for the cotype specimen of hanauerite. Both diffractometers are equipped with CCD detectors, and  $\text{MoK}\alpha$  radiation was used in both cases. The crystal structures were solved via direct methods. Data collection and structure refinement details are summarized and discussed below, in Section 3.3.

Attempts to measure the micro-indentation hardness value were unsuccessful because hanauerite crystals are tiny and brittle (and not embedded in a rock matrix) that causes the cracking during the indentation of the Vickers diamond pyramid. Density could not be measured because crystals are too small for volumetric methods and because of the lack of heavy liquids of necessary density.

## 3. Results

### 3.1. Optical Data

Under the microscope in reflected light, the holotype hanauerite is grey, and pleochroism was not observed. Bi-reflectance is very weak,  $\Delta R = 1.1\%$  (589 nm). Anisotropism is weak. Internal reflections were not observed. The reflectance values are given in Table 1.

**Table 1.** The reflectance data of hanauerite from the Schöne Aussicht Mine.

$\lambda$ , nm	$R_1$ , %	$R_2$ , %	$\lambda$ , nm	$R_1$ , %	$R_2$ , %
400	14.3	13.1	560	11.6	10.5
420	13.9	12.8	580	11.3	10.2
440	13.5	12.4	<b>589</b>	<b>11.2</b>	<b>10.1</b>
460	13.2	12.1	600	11.1	10.0
<b>470</b>	<b>13.1</b>	<b>11.9</b>	620	10.9	9.8
480	12.9	11.8	640	10.7	9.6
500	12.6	11.4	<b>650</b>	<b>10.6</b>	<b>9.5</b>
520	12.2	11.1	660	10.5	9.4
540	11.9	10.8	680	10.3	9.2
<b>546</b>	<b>11.8</b>	<b>10.7</b>	700	10.1	9.1

The values for wavenumbers ( $\lambda$ ) recommended by the IMA Commission on Ore Microscopy (COM) are given in bold type.

### 3.2. Chemical Composition

The chemical composition of hanauerite in wt.% is given in Table 2.

**Table 2.** Chemical composition of hanauerite.

Sample Constituent	Holotype (Schöne Aussicht Mine)		Cotype (Friedrichsseggen Mine)	
	Wt.% *	Range	Wt.% *	Range
Ag	22.42	21.83–23.22	23.26	22.84–23.61
Hg	43.94	43.02–44.52	43.05	42.74–43.30
S	7.12	6.92–7.34	7.42	7.17–7.76
Cl	0.20	0.12–0.24	-	-
Br	3.26	2.69–4.22	4.41	3.92–5.24
I	23.23	21.12–24.04	21.39	20.41–22.04
Total	100.17		99.53	

\* Averaged for five spot analyses for holotype and three spot analyses for cotype; dash means that the Cl content is below detection limit.

The empirical formulae calculated on the sum of all atoms = 4 *apfu* are:

holotype (Schöne Aussicht Mine):  $\text{Ag}_{0.95}\text{Hg}_{1.00}\text{S}_{1.01}(\text{I}_{0.83}\text{Br}_{0.19}\text{Cl}_{0.03})_{\Sigma 1.05}$ ;

cotype (Friedrichsseggen Mine):  $\text{Ag}_{0.97}\text{Hg}_{0.97}\text{S}_{1.05}(\text{I}_{0.76}\text{Br}_{0.25})_{\Sigma 1.01}$ .

The simplified formula of hanauerite can be written as  $\text{AgHgS}(\text{I},\text{Br})$ . The idealized, end-member formula  $\text{AgHgSI}$  requires Ag 23.08, Hg 42.91, S 6.86, I 27.15; total 100 wt%.

### 3.3. X-ray Crystallography and Crystal Structure Determination

Powder XRD data of the holotype hanauerite are given in Table 3. The orthorhombic unit cell parameters calculated from the powder data are:  $a = 9.931(2)$ ,  $b = 4.622(1)$ ,  $c = 9.909(3)$  Å, and  $V = 454.8(3)$  Å<sup>3</sup>. The calculations of intensities ( $I_{\text{calc}}$  in Table 3) were performed using a standard STOE WinXPOW programme.

**Table 3.** Powder X-ray diffraction data ( $d$  in Å) of hanauerite from the Schöne Aussicht Mine.

$I_{\text{obs}}$	$d_{\text{obs}}$	$I_{\text{calc}}$ *	$d_{\text{calc}}$ **	$h k l$
20	9.88	16	9.891	001
15	6.99	11	7.008	101
3	4.932	0.5, 0.5	4.966, 4.945	200, 002
13	4.439	14	4.438	201
32	4.185	27	4.187	011
58	3.857	56	3.858	111
11	3.377	6, 3	3.383, 3.377	210, 012
16	3.300	10	3.297	003
22	3.201	21	3.201	211
20	3.138	22, 4	3.139, 3.129	301, 103
100	2.793	100	2.792	212
3	2.685	1	2.684	013
10	2.594	12	2.591	113
30	2.477	18, 24	2.483, 2.473	400, 004
10	2.332	7	2.336	303
22	2.312	30	2.311	020
6	2.217	3, 1	2.219, 2.214	402, 204

Table 3. Cont.

$I_{\text{obs}}$	$d_{\text{obs}}$	$I_{\text{calc}}^*$	$d_{\text{calc}}^{**}$	$hkl$
6	2.189	1, 4, 1	2.195, 2.187, 2.181	121, 410, 014
7	2.133	4, 3	2.136, 2.130	411, 114
5	2.050	3	2.050	221
13	1.999	11, 6	2.000, 1.996	412, 214
2	1.950	0.5, 0.5	1.948, 1.940	501, 105
4	1.895	4	1.892	023
6	1.862	8, 1	1.861, 1.859	321, 123
5	1.824	3, 3	1.823, 1.819	413, 015
4	1.791	6, 4	1.795, 1.789	511, 115
5	1.771	1, 4	1.770, 1.768	322, 223
8	1.754	9	1.752	404
6	1.708	4	1.708	215
12	1.692	10, 13	1.692, 1.688	420, 024
5	1.643	4, 4	1.643, 1.638	323, 414
3	1.598	2, 0.5, 2	1.601, 1.599, 1.597	422, 224, 513
2	1.557	2, 1	1.558, 1.553	610, 016
2	1.503	1, 3	1.505, 1.505	423, 131
6	1.484	5, 7	1.486, 1.482	612, 216
3	1.468	1, 1	1.468, 1.467	514, 415
1	1.440	1	1.438	225
5	1.411	10, 0.5	1.410, 1.409	232, 613
4	1.400	0.5, 0.5, 8	1.402, 1.399, 1.396	505, 107, 424
1	1.383	1	1.382	133
2	1.373	0.5, 0.5, 1	1.376, 1.373, 1.370	604, 406, 523
1	1.343	1, 1, 1	1.346, 1.344, 1.341	620, 711, 515
2	1.319	2, 2	1.318, 1.316	614, 416
1	1.297	0.5, 0.5, 0.5	1.299, 1.298, 1.296	622, 431, 134
2	1.266	2, 1	1.266, 1.265	432, 234
2	1.244	1, 1	1.244, 1.242	326, 800
2	1.216	0.5, 1	1.217, 1.215	433, 035
2	1.208	2, 1, 0.5	1.208, 1.206, 1.206	531, 135, 027

\* For the calculated pattern, only reflections with intensities  $\geq 0.5$  are given; \*\*, the unit cell parameters calculated from single-crystal data. The strongest reflections are marked in bold type.

The crystal structure was studied on single crystals for both holotype and cotype specimens of hanauerite. The structures were solved in the frame of the orthorhombic space group *Pmma* via direct methods and refined with the use of SHELX software package [20] and to  $R = 0.0416$  on the basis of 607 independent reflections with  $I > 2\sigma(I)$  (holotype) and to  $R = 0.0544$  on the basis of 635 independent reflections with  $I > 2\sigma(I)$  (cotype). Crystal data and details on data collection and structure refinement are given in Table 4, coordinates and equivalent thermal displacement parameters of atoms in Table 5, and selected interatomic distances in Table 6. Crystallographic information files (CIFs) are available as Supplementary Materials.

**Table 4.** Crystal data, data collection information, and structure refinement details of hanauerite.

Locality	Friedrichssegen Mine	Schöne Aussicht Mine
Formula, from structure refinement	AgHgS(I <sub>0.75</sub> Br <sub>0.25</sub> )	
Formula weight	455.67	
Temperature, K	293(2)	
Radiation and wavelength, Å	MoK $\alpha$ ; 0.71073	
Crystal system, space group, Z	Orthrhombic, <i>Pmma</i> , 4	
Unit cell dimensions, Å/°	<i>a</i> = 9.9276(8) <i>b</i> = 4.6209(2) <i>c</i> = 9.9006(4)	<i>a</i> = 9.932(4) <i>b</i> = 4.6219(19) <i>c</i> = 9.891(4)
<i>V</i> , Å <sup>3</sup>	454.19(5)	454.0(3)
Absorption coefficient $\mu$ , mm <sup>-1</sup>	45.61	45.63
<i>F</i> <sub>000</sub>	766	
Crystal size, mm	0.02 × 0.02 × 0.05	0.01 × 0.01 × 0.15
Diffractometer	Xcalibur S CCD	Bruker Kappa APEX DUO CCD
$\theta$ range for data collection, °/Collection mode	2.91–28.22/full sphere	
Index ranges	$-13 \leq h \leq 13$ , $-6 \leq k \leq 6$ , $-13 \leq l \leq 13$	$-11 \leq h \leq 13$ , $-6 \leq k \leq 6$ , $-13 \leq l \leq 13$
Reflections collected	7457	4037
Independent reflections	667 ( <i>R</i> <sub>int</sub> = 0.0654)	666 ( <i>R</i> <sub>int</sub> = 0.0992)
Independent reflections with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	635	607
Data reduction	CrysAlisPro, Agilent Technologies, v. 1.171.37.35 [21]	Bruker APEX-2 [22]
Absorption correction	Gaussian	Multi-scan
Structure solution	direct methods	
Refinement method	full-matrix least-squares on <i>F</i> <sup>2</sup>	
Number of refined parameters	37	35
Final <i>R</i> indices ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	<i>R</i> 1 = 0.0544, w <i>R</i> 2 = 0.0984	<i>R</i> 1 = 0.0416, w <i>R</i> 2 = 0.1040
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0586, w <i>R</i> 2 = 0.0995	<i>R</i> 1 = 0.0469, w <i>R</i> 2 = 0.1068
GoF	1.447	1.142
Largest diff. peak and hole, e/Å <sup>3</sup>	3.01 and −2.28	2.15 and −2.61

**Table 5.** Coordinates and equivalent displacement parameters (*U*<sub>eq</sub>, in Å<sup>2</sup>) of atoms, site multiplicities (*Q*), and site occupancy factors (s.o.f.) of hanauerite. Data for the sample from the Friedrichssegen Mine are given in the first line of each row and data for the sample from the Schöne Aussicht Mine in the second line of each row.

Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>	<i>Q</i>	s.o.f.
Hg(1)	0.25	0.5	0.75709(13)	0.0392(3)	2	1
	0.25	0.5	0.75732(10)	0.0413(3)		
Hg(2)	0.0	0.5	0.5	0.0402(4)	2	1
	0.0	0.5	0.5	0.0421(3)		
Ag'	0.0914(17)	0.0	0.2230(14)	0.059(3)	4	Ag <sub>0.50</sub> Ag <sub>0.744(11)</sub>
	0.0827(5)	0.0	0.2196(5)	0.0651(12) *		
Ag''	0.0521(17)	0.0	0.1885(16)	0.088(5)	4	Ag <sub>0.50</sub> Ag <sub>0.256(11)</sub>
	0.0388(14)	0.0	0.1644(15)	0.0651(12) *		
I(1)	0.25	0.0	0.4769(2)	0.0303(7)	2	I <sub>0.54(2)</sub> Br <sub>0.46(2)</sub> I <sub>0.57(2)</sub> Br <sub>0.43(2)</sub> **
	0.25	0.0	0.47676(17)	0.0324(6)		
I(2)	0.25	0.0	0.98976(17)	0.0336(6)	2	I <sub>0.97(3)</sub> Br <sub>0.03(3)</sub> I <sub>0.94(2)</sub> Br <sub>0.06(2)</sub> **
	0.25	0.0	0.99018(13)	0.0349(5)		
S	0.4876(5)	0.5	0.7387(5)	0.0297(10)	4	1
	0.4881(4)	0.5	0.7386(4)	0.0285(7)		

\* Displacement parameters were restricted to be equal. \*\* Minor Cl impurity (see Table 1) was ignored during the refinement.



**Table 6.** Selected interatomic distances (Å) in the structure of hanauerite.

Friedrichsseggen Mine		Schöne Aussicht Mine	
Hg(1)–S	2.366(5) × 2	Hg(1)–S	2.372(4) × 2
–I(2)	3.2626(14) × 2	–I(2)	3.2627(15) × 2
–I(1)	3.6102(19) × 2	–I(1)	3.6113(19) × 2
Hg(2)–S	2.366(5) × 2	Hg(2)–S	2.363(4) × 2
–I(1)	3.3986(2) × 4	–I(1)	3.3998(10) × 4
Ag'–S	2.558(8) × 2	Ag'–S	2.529(2) × 2
–I(2)	2.795(17)	–I(2)	2.813(3)
–I(1)	2.966(12)	–I(1)	3.038(7)
Ag''–S	2.504(8) × 2	Ag''–S	2.552(5) × 2
–I(2)	2.780(19)	–I(2)	2.715(10)
–I(1)	3.466(14)	–I(1)	3.734(14)
–I(2)	3.479(14)	–I(2)	3.250(17)

## 4. Discussion

### 4.1. Crystal Structure of Hanauerite

The crystal structure of hanauerite (Figure 3) is very close to those known for its synthetic analogue AgHgSI and isostructural compounds CuHgSeBr and AgHgSBr [23], as well as HT phases CuHgSbCl [24] and CuHgSBr [25]. These synthetic compounds crystallize in the same orthorhombic space group *Pnma* and are close to hanauerite in unit cell dimensions. Two crystallographically non-equivalent Hg sites are present in the structure of hanauerite (as well as in the abovementioned synthetic compounds) and each Hg<sup>2+</sup> cation forms covalent bonds with two sulphur atoms. The parameters of these bonds are as follows: distances 2.366(5) Å for both Hg sites and S–Hg–S angles 171.2° for Hg(1) and 180.0° for Hg(2) (cotype) and Hg(1)–S 2.372(4) Å and Hg(2)–S 2.363(4) Å and S–Hg–S angles 171.1° for Hg(1) and 180.0° for Hg(2) (holotype). Hg and S atoms form “crankshaft-type” chains along the *a* axis (Figure 4). The coordination environment of Hg atoms is complemented by elongated Hg–I bonds (Table 6). Thus, distorted Hg-centred octahedra are formed (Figure 5). Both I(1) and I(2) sites are iodine-dominant; the refined I:Br ratios are I<sub>0.54</sub>Br<sub>0.46</sub> for the I(1) site and I<sub>0.97</sub>Br<sub>0.03</sub> for the I(2) site (cotype) and I<sub>0.57</sub>Br<sub>0.43</sub> for the I(1) site and I<sub>0.94</sub>Br<sub>0.06</sub> for the I(2) site (holotype; minor Cl impurity was ignored during the refinement), both resulting in the total I:Br ratio of 3:1 that is in good agreement with electron microprobe data (Table 2). Hg(2)-centred octahedra share I(1)–I(1) edges to form the (001) layers, while Hg(1)-centred octahedra share I(1)–I(2) common edges to form the chains running along [010]. The chains are connected with the corrugated octahedral layers via common faces of octahedra from both sides of each layer (Figure 6). Ag<sup>+</sup> cations are located between the octahedral layers in hanauerite. Unlike synthetic compounds AgHgSI and AgHgSBr [23], the Ag site in both structurally studied samples of hanauerite is split into two subsites labelled as Ag' and Ag'' (Table 5). The Ag'–Ag'' distance is 0.52 Å in the cotype and 0.70 Å in the holotype sample. Their occupancy factors are approximately equal (the refinement presented s.o.f. values of 0.49 for both sites; thus, they were fixed at 0.5 for each) in cotype, while in holotype, the Ag' site is 74% occupied and Ag'' is 26% occupied (Table 5). The location of the Ag' site in hanauerite is very close to that of the non-split Ag site in synthetic AgHgSI and AgHgSBr. In all these sulphohalides, this position is coordinated by two S atoms and two halogen atoms, thus centring the distorted tetrahedron. The Ag''-centred polyhedron in hanauerite has two short distances Ag''–S, one longer Ag''–I distance, and two strongly elongated Ag''–I distances (Table 6). Coordination environments of Ag sites in hanauerite are shown in Figure 7.

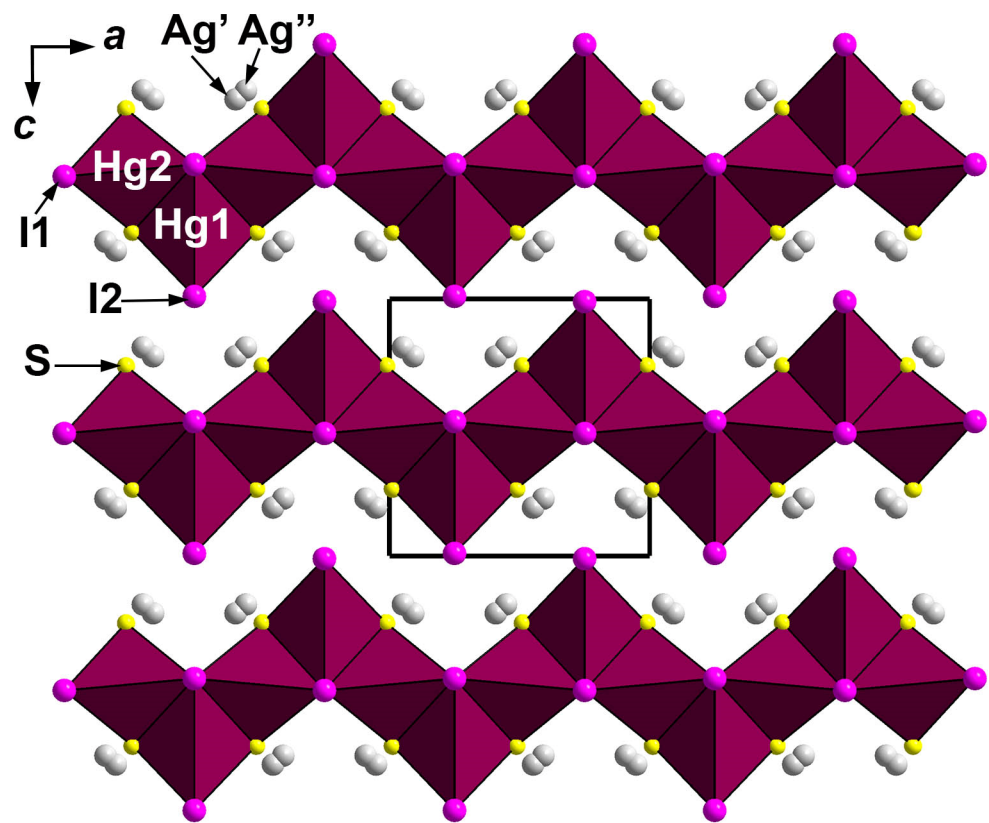


Figure 3. The crystal structure of hanauerite. The unit cell is outlined.

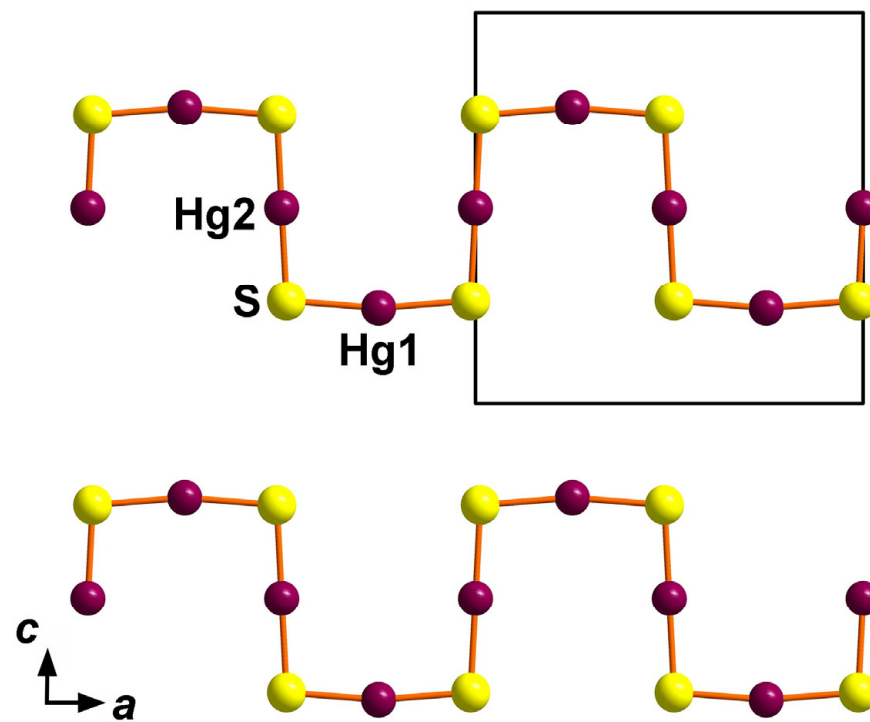
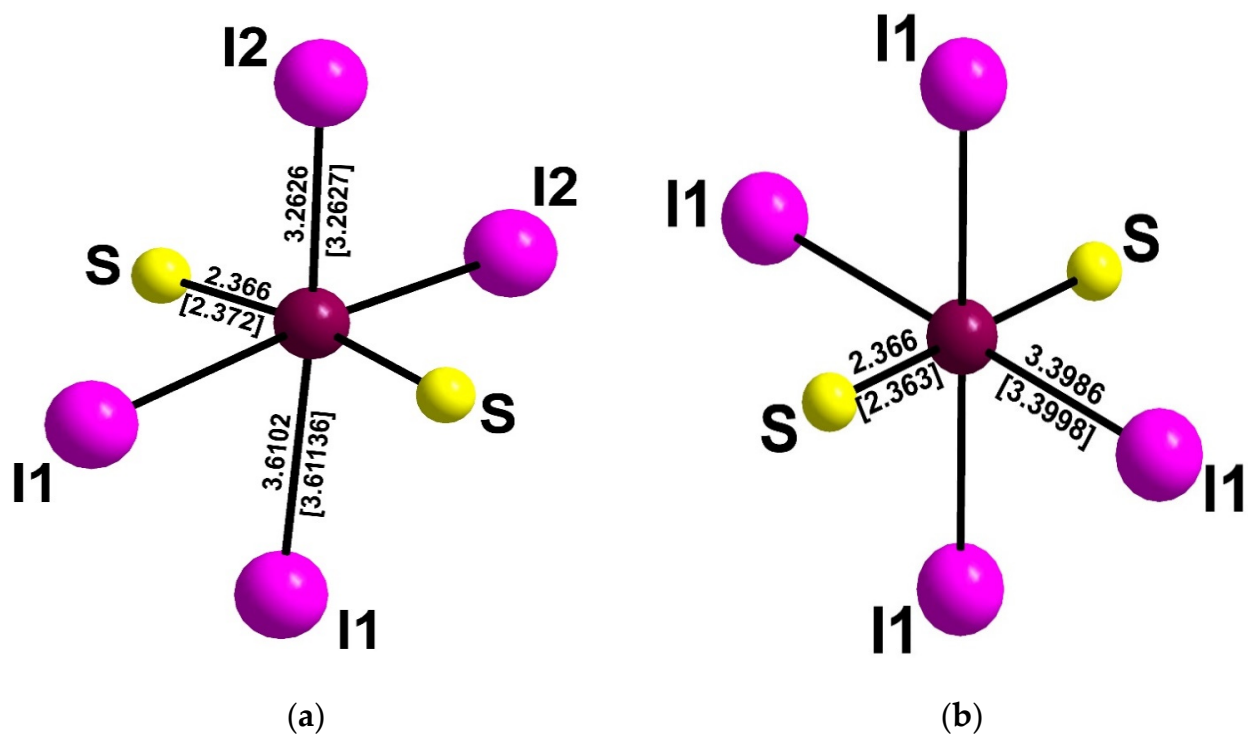
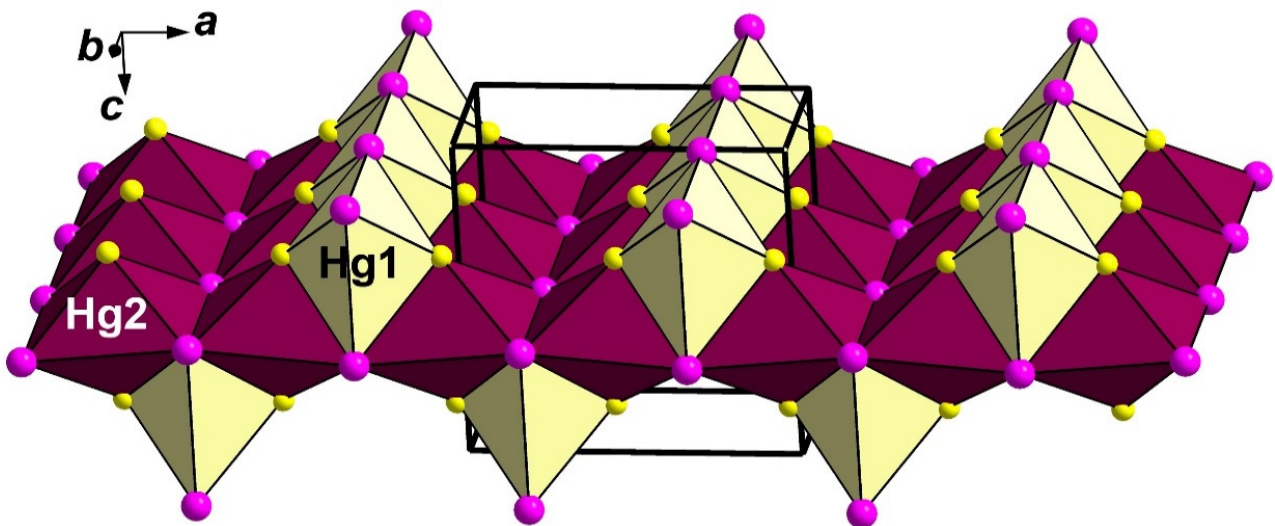


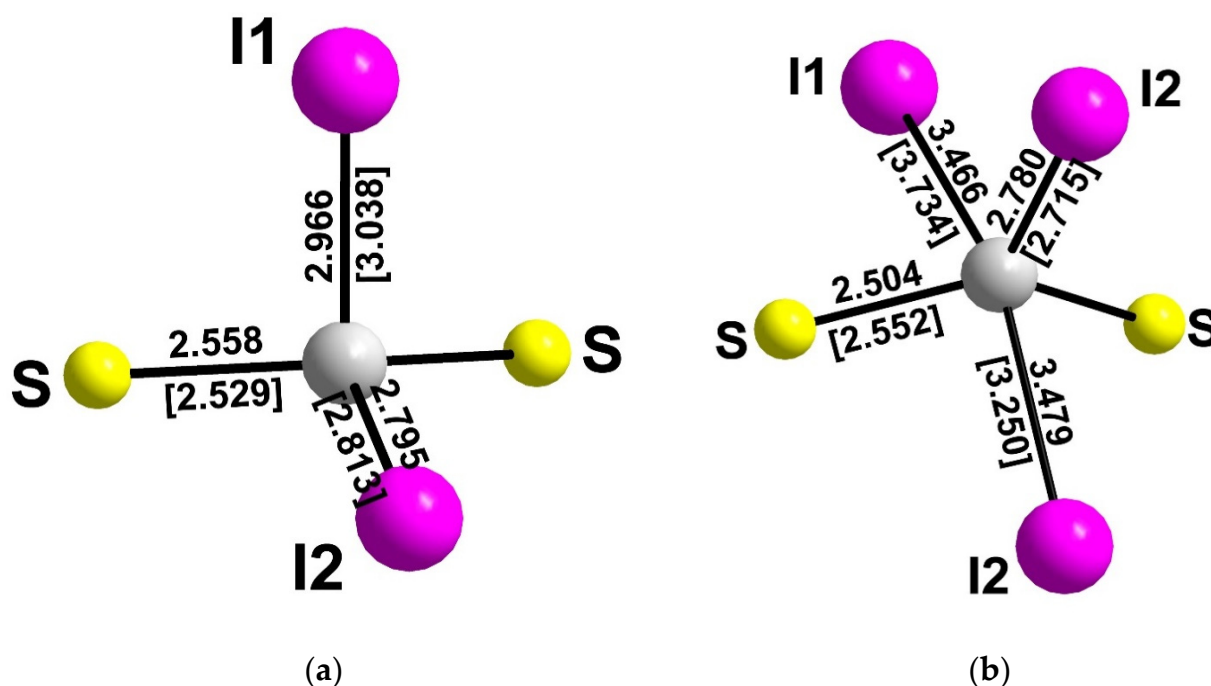
Figure 4. "Crankshaft-type" Hg-S chains in the structure of hanauerite. The unit cell is outlined.



**Figure 5.** Coordination environments of Hg(1) (a) and Hg(2) (b) sites in the structure of hanauerite. The distances (in Å) for the holotype sample are given in square brackets and for the cotypic sample without brackets.



**Figure 6.** Octahedral layer built by edge-sharing Hg(2)-octahedra (central part) and chains of Hg(1) octahedra in the structure of hanauerite (for better clarity Hg(1)- and Hg(2)-centred octahedra are illustrated in different colours).



**Figure 7.** Coordination environments of Ag' (a) and Ag'' (b) sites in the structure of hanauerite. The distances (in Å) for the holotype specimen are given in square brackets and for the cotype specimen without brackets.

#### 4.2. Common Crystal Chemical Features of Natural Mercury Sulphohalides

In minerals, the octahedral coordination of  $\text{Hg}^{2+}$  by sulphur and halogen atoms was reported for capgaronnite [11], perroudite [15], and the synthetic analogues of corderoite [26] and radtkeite [9,10]. Distorted  $\text{Hg}^{2+}$ -centred octahedra with two short Hg–S bonds and four elongated Hg–Hal (Hal = Cl, Br, I) were found in the synthetic analogue of grechishchevite [6,7]. Pervukhina et al. [27,28] reported a distorted octahedral coordination of Hg atoms in structures of two polymorphic modifications of  $\text{Hg}_3\text{S}_2\text{Cl}_{2-x}\text{Br}_x$  ( $x \approx 0.5$ ) obtained during the attempts to synthesize an analogue of lavrentievite and in two polymorphic modifications of  $\text{Hg}_3\text{S}_2\text{Br}_{2-x}\text{Cl}_x$  ( $x \approx 0.5$ ) obtained during the attempts to synthesize an analogue of arzakite. In the structure of capgaronnite,  $\text{HgS}_2(\text{Cl},\text{Br})_4$  octahedra form (010) straight layers connected by the pairs of Ag-centred tetrahedra, whereas in perroudite, face-sharing  $\text{Hg}^{2+}$  octahedra form triple chains that are further linked by double chains of Hg-centred octahedra to the framework. In both hanauerite and capgaronnite, Hg–S chains are planar but essentially different in topology: the zigzag chain is reported for capgaronnite, and the “crankshaft-type” chain for hanauerite and structurally close and related synthetic compounds. At the same time, in perroudite, these chains are helical as well as cinnabar in shape. Structural relationships of perroudite with capgaronnite, corderoite, cinnabar, and synthetic  $\text{HgCuSCl}$ ,  $\beta\text{-Hg}_3\text{S}_2\text{Br}_2$ , and  $\text{Hg}_3\text{S}_2\text{I}_3$  are discussed in [15] and references therein.

## 5. Conclusions

This paper is devoted to the new mineral hanauerite, ideally  $\text{AgHgSI}$ , the first natural mercury-bearing sulphohalide in which iodine is the only species-defining halogen. It is an analogue in the formulae for capgaronnite and iltisite, both ideally  $\text{AgHgSCl}$ ; however, they are significantly different in terms of structure and, in general, hanauerite has no structural analogues among minerals.

Hanauerite possesses the same main crystal chemical features as typical for mercury sulphohalides. The cations  $\text{Hg}^{2+}$  occupy strongly distorted octahedra with two short Hg–S bonds (Hg and S atoms build “crankshaft-type” chains) and four strongly elongated Hg–I bonds. The Hg-centred octahedra are connected via common edges and faces to form

corrugated layers. Such linkage is also characteristic for other compounds with layered or framework structures built by Hg-centred octahedra.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst13081218/s1>, The crystallographic information files (CIF) are in Supplementary Files.

**Author Contributions:** Conceptualization, I.V.P., N.V.Z. and S.N.B.; methodology, N.V.Z., S.N.B., I.V.P. and D.Y.P.; investigation, I.V.P., N.V.Z., S.N.B., A.A.A. and Y.S.P.; writing—original draft preparation, I.V.P. and N.V.Z.; writing—review and editing, I.V.P., N.V.Z., S.N.B. and D.Y.P.; mineral collection and providing samples, G.M., J.D. and G.B. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Data Availability Statement:** Not applicable.

**Acknowledgments:** The research has been carried out using facilities of XRD Research Centre of St. Petersburg State University in part of XRD studies of holotype hanauerite. We are grateful to reviewers for useful comments.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Foord, E.E.; Berendsen, P.; Storey, L.O. Corderoite, first natural occurrence of  $\alpha$ - $\text{Hg}_3\text{S}_2\text{Cl}_2$ , from the Cordero mercury deposit, Humboldt County, Nevada. *Am. Mineral.* **1974**, *59*, 652–655.
2. Vasil'ev, V.I.; Pal'chik, N.A.; Grechishchev, O.K. Lavrentievite and arzakite, new natural sulfohalogenides of mercury. *Geol. Geofiz.* **1984**, *7*, 54–63. (In Russian)
3. Vasil'ev, V.I.; Lavrent'ev, Y.G.; Pal'chik, N.A. New data on arzakite and lavrentievite. *Dokl. Akad. Nauk. SSSR* **1986**, *290*, 948–951. (In Russian)
4. McCormack, J.K.; Dickson, F.W. Kenhsuite,  $\gamma$ - $\text{Hg}_3\text{S}_2\text{Cl}_2$ , a new mineral species from the McDermit mercury deposit, Humboldt County, Nevada. *Can. Mineral.* **1998**, *36*, 201–206.
5. Vasil'ev, V.I.; Usova, L.V.; Pal'chik, N.A. Grechishchevite— $\text{Hg}_3\text{S}_2(\text{Br}, \text{Cl}, \text{I})_2$ —A new supergene mercury sulfohalide. *Geol. Geofiz.* **1989**, *30*, 61–69. (In Russian)
6. Pervukhina, N.V.; Vasil'ev, V.I.; Borisov, S.V.; Magarill, S.A.; Naumov, D.Y. The crystal structure of a polymorph of  $\text{Hg}^{2+}_3\text{S}_2\text{Br}_{1.0}\text{Cl}_{0.5}\text{I}_{0.5}$ . *Can. Mineral.* **2003**, *41*, 1445–1453. [[CrossRef](#)]
7. Pervukhina, N.V.; Borisov, S.V.; Magarill, S.A.; Naumov, D.Y.; Vasiliev, V.I.; Nenashev, B.G. Crystal structure of the synthetic analogue of grechishchevite and  $\text{Hg-X}$  ( $X = \text{S}, \text{Se}, \text{Te}$ ) bond topology in mercury chalcogen halides. *J. Struct. Chem.* **2004**, *45*, 437–445. [[CrossRef](#)]
8. McCormack, J.K.; Dickson, F.W.; Leshendok, M.P. Radtkeite,  $\text{Hg}_3\text{S}_2\text{ClI}$ , a new mineral from the McDermit mercury deposit, Humboldt County, Nevada. *Am. Mineral.* **1991**, *76*, 1715–1721.
9. Pervukhina, N.V.; Vasil'ev, V.I.; Naumov, D.Y.; Borisov, S.V.; Magarill, S.A. The crystal structure of synthetic radtkeite,  $\text{Hg}_3\text{S}_2\text{ClI}$ . *Can. Mineral.* **2004**, *42*, 87–94. [[CrossRef](#)]
10. Pervukhina, N.V.; Borisov, S.V.; Magarill, S.A.; Naumov, D.Y.; Vasiliev, V.I.; Nenashev, B.G. Crystal structure of the synthetic analog of radtkeite  $\text{Hg}_3\text{S}_2\text{Cl}_{1.00}\text{I}_{1.00}$ . *J. Struct. Chem.* **2004**, *45*, 720–723. [[CrossRef](#)]
11. Mason, B.; Mumme, W.G.; Sarp, H. Capgaronnite,  $\text{HgSAg}(\text{Cl}, \text{Br}, \text{I})$ , a new sulfide-halide mineral from Var, France. *Am. Mineral.* **1992**, *77*, 197–200.
12. Sarp, H.; Sanz-Gysler, J.; Perroud, P. Iltisite,  $\text{HgSAg}(\text{Cl}, \text{Br})$ , un nouveau minéral de la mine de Cap Garonne, Var (France), polymorphe de la capgaronnite. *Arch. Des Sci.* **1997**, *50*, 1–5.
13. Sarp, H.; Birch, W.D.; Hlava, P.F.; Pring, A.; Sewell, D.K.; Nickel, E.H. Perroudite, a new sulfide-halide of Hg and Ag from Cap-Garonne, Var, France, and from Broken Hill, New South Wales, and Coppin Pool, Western Australia. *Am. Mineral.* **1987**, *72*, 1251–1256.
14. Mumme, W.G.; Nickel, E.H. Crystal structure and crystal chemistry of perroudite: A mineral from Coppin Pool, Western Australia. *Am. Mineral.* **1987**, *72*, 1257–1262.
15. Keller, P.; Lissner, F.; Schleid, T. Single-crystal structure determination of perroudite,  $\text{Hg}_5\text{Ag}_4\text{S}_5(\text{I}, \text{Br})_2\text{Cl}_2$ , from Tsumeb (Namibia), and its structural relationships to other sulfide halides of mercury and cinnabar. *Neues Jahrb. Mineral. Abh.* **2005**, *181*, 1–9. [[CrossRef](#)]
16. Pekov, I.V.; Zubkova, N.V.; Britvin, S.N.; Agakhanov, A.A.; Polekhovskiy, Y.S.; Pushcharovsky, D.Y.; Möhn, G.; Desor, J.; Blass, G. Hanauerite, IMA 2018-045. CNMNC Newsletter No. 45, October 2018, page 1226. *Mineral. Mag.* **2018**, *82*, 1225–1232.
17. Buchert, D.E. Die Grube Schöne Aussicht bei Dernbach im Westerwald. *Miner. Welt.* **2012**, *23*, 36–53.

18. Schnorrer, G.; Christ, H.G.; Hiller, V.; Frohwein, J. Die Minerale von der ehemaligen Grube Friedrichsseggen des Emser Gangzuges bei Bad Ems/Rheinland-Pfalz. *Der Aufschluss* **2004**, *55*, 65–104.
19. Britvin, S.N.; Dolivo-Dobrovolsky, D.V.; Krzhizhanovskaya, M.G. Software for processing the X-ray powder diffraction data obtained from the curved image plate detector of Rigaku RAXIS Rapid II diffractometer. *Zapiski RMO* **2017**, *146*, 3–104. (In Russian)
20. Sheldrick, G.M. A short history of SHELX. *Acta Cryst.* **2008**, *A64*, 112–122. [[CrossRef](#)]
21. Agilent Technologies. *CrysAlisPro Software System, Version 1.171.37.35*; Agilent Technologies: Oxford, UK, 2014.
22. Bruker AXS APEX-2; Bruker Inc.: Madison, WI, USA, 2005.
23. Beck, J.; Keller, H.L.; Rompel, M.; Wimbart, L. Hydrothermalsynthese und Kristallstruktur der Münzmetall-Quecksilber-Chalkogenidhalogenide CuHgSeBr, AgHgSBr und AgHgSI. *Z. Anorg. Allg. Chem.* **2001**, *627*, 2289–2294. [[CrossRef](#)]
24. Moro'oka, M.; Ohki, H.; Yamada, K.; Okuda, T. Crystal structure of high temperature phase and ionic conductivity mechanism of CuHgSX (X = Cl, Br). *Bull. Chem. Soc. Jpn.* **2003**, *76*, 2111–2115. [[CrossRef](#)]
25. Beck, J.; Rompel, M. Über Münzmetall-Quecksilber-Chalkogenidhalogenide. II Hydrothermalsynthese, Kristallstruktur und Phasenumwandlung von CuHgSCl und CuHgSBr. *Z. Anorg. Allg. Chem.* **2003**, *629*, 421–428. [[CrossRef](#)]
26. Frueh, A.J.; Gray, N. Confirmation and refinement of the structure of Hg<sub>3</sub>S<sub>2</sub>Cl<sub>2</sub>. *Acta Cryst.* **1968**, *1968*, B24, 156–157. [[CrossRef](#)]
27. Pervukhina, N.V.; Vasiliev, V.I.; Magarill, S.A.; Borisov, S.V.; Naumov, D.Y. Crystal chemistry of mercury sulfohalides of composition Hg<sub>3</sub>S<sub>2</sub>Hal<sub>2</sub> (Hal: Cl, Br). I. Crystal structures of two polymorphic modifications of Hg<sub>3</sub>S<sub>2</sub>Cl<sub>2-x</sub>Br<sub>x</sub> (x ≈ 0.5). *Can. Mineral.* **2006**, *44*, 1239–1246. [[CrossRef](#)]
28. Pervukhina, N.V.; Vasiliev, V.I.; Magarill, S.A.; Borisov, S.V.; Naumov, D.Y. Crystal chemistry of mercury sulfohalides of composition Hg<sub>3</sub>S<sub>2</sub>Hal<sub>2</sub> (Hal: Cl, Br). II. Crystal structures of two polymorphic modifications of Hg<sub>3</sub>S<sub>2</sub>Br<sub>2-x</sub>Cl<sub>x</sub> (x ≈ 0.5). *Can. Mineral.* **2006**, *44*, 1247–1255. [[CrossRef](#)]

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.