



## Article

# Vrančiceite, $\text{Cu}_{10}\text{Hg}_3\text{S}_8$ , a new Cu–Hg sulfide mineral from Vrančice, Czech Republic

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### Abstract

Vrančiceite is a new mineral species discovered in a sample collected from the old mine dumps of the abandoned Vrančice deposit near Příbram, central Bohemia, Czech Republic. Vrančiceite occurs as rare anhedral grains, up to 100  $\mu\text{m}$  in size, in a calcite gangue, associated with cinnabar, djurleite, galena and hedyphane. Vrančiceite is black, with metallic lustre. Mohs hardness is *ca.* 2–3, calculated density is 6.652  $\text{g}\cdot\text{cm}^{-3}$ . In reflected light, vrančiceite is light grey with a yellowish shade; bireflectance, pleochroism and anisotropy are all weak. Internal reflections were not observed. Reflectance values for the four Commission on Ore Mineralogy wavelengths of vrančiceite in air [ $R_{\text{max}}$ ,  $R_{\text{min}}$  (%) ( $\lambda$  in nm)] are: 33.6, 31.2 (470); 33.9, 30.6 (546); 31.1, 30.0 (589); and 32.1, 29.1 (650). The empirical formula, based on electron-microprobe analyses, is  $\text{Cu}_{10.11(4)}\text{Ag}_{0.01(1)}\text{Hg}_{2.87(4)}\text{Sb}_{0.01(1)}\text{Bi}_{0.01(1)}\text{S}_{7.99(8)}$ . The ideal formula is  $\text{Cu}_{10}\text{Hg}_3\text{S}_8$  ( $Z=2$ ), which requires (in wt.%) Cu 42.54, Hg 40.29 and S 17.17, total 100.00. Vrančiceite is triclinic,  $P\bar{1}$ , with unit-cell parameters  $a=7.9681(2)$ ,  $b=9.7452(3)$ ,  $c=10.0710(3)$  Å,  $\alpha=77.759(1)$ ,  $\beta=76.990(1)$ ,  $\gamma=79.422(1)^\circ$ ,  $V=737.01(4)$  Å<sup>3</sup> and  $Z=2$ . The strongest reflections of the calculated powder X-ray diffraction pattern [ $d$ , Å (I)  $hkl$ ] are: 3.354 (76)  $\bar{2}01$ , 3.111 (68) 222, 2.833 (100) 213, 2.733 (93) 231, 2.705 (76)  $\bar{2}\bar{1}1$  and 2.647 (71)  $\bar{2}\bar{1}\bar{2}$ . According to the single-crystal X-ray diffraction data ( $R_1=0.0262$ ), the crystal structure of vrančiceite can be described as comprising Cu–S layers, connected through  $\text{CuS}_3$  polyhedra, giving rise to a three-dimensional framework with channels running along the *a* axis and hosting linearly coordinated Hg atoms. Structural relations with gortdrumite are discussed. Vrančiceite is named after its type locality, the Vrančice deposit near Příbram. The mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA2022–114).

**Keywords:** vrančiceite, new mineral, sulfide, copper, mercury, crystal structure, Vrančice, Czech Republic

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### Introduction

In 1988, gortdrumite, with the ideal formula  $(\text{Cu},\text{Fe})_6\text{Hg}_2\text{S}_5$ , was described from the Gortdrum mine, Monard, County Tipperary, Ireland (Steed, 1983). At that time, its crystal structure remained unknown. During the systematic investigation of ore minerals from the Příbram area, Czech Republic, Škácha and Sejkora (2013) identified at the Vrančice deposit a mineral having a gortdrumite-like chemical composition, the only difference being represented by the absence of Fe. Indeed, these authors described this phase as an Fe-free gortdrumite-like mineral, with empirical formula  $(\text{Cu}_{6.26}\text{Ag}_{0.01})_{\Sigma 6.27}\text{Hg}_{1.78}\text{S}_{4.95}$ . Recently, Bindi *et al.* (2018) solved the crystal structure of gortdrumite using a sample from Leogang, Salzburg, Austria. It is characterised by an Fe-dominant site, and the chemical formula was revised to  $\text{Cu}_{24}\text{Fe}_2\text{Hg}_9\text{S}_{23}$  ( $Z=1$ ). It was then obvious that the mineral from Vrančice is different from gortdrumite. Thus, a crystal-chemical investigation was undertaken, which allowed

for the solution of its crystal structure and the proposal of the new mineral vrančiceite.

This new mineral and its name (symbol Vrc) were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA2022-114, Sejkora *et al.*, 2023). Vrančiceite is named after its type locality, the Vrančice deposit near Příbram, Czech Republic. The holotype material (polished section) is deposited in the mineralogical collection of the Department of Mineralogy and Petrology of the National Museum, Prague, Czech Republic (catalogue number P1P 42/2022); the cotype material is in the collection of the Mining Museum Příbram, Czech Republic (catalogue number 2/2023) and the crystal used for the single-crystal X-ray diffraction study is kept in the mineralogical collection of the Museo di Storia Naturale of the Università di Pisa, Via Roma 79, Calci (PI), Italy, under catalogue number 20024.

### Occurrence and mineral description

#### Occurrence

Vrančiceite was only found in one specimen,  $3.5 \times 5 \times 4$  cm in size, collected by one of us (PŠ) in 2012 from the dumps of an

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old mine exploited in the 16<sup>th</sup> Century on Vraněč hill, north of Vrančice village (49°37'10.71"N, 14°02'51.69"E), central Bohemia, Czech Republic. This mine exploited the surficial portion of the most important Vrančice vein, Beschert Glück, known as the Pošepný vein from the 19<sup>th</sup> Century. The last period of mining focused on Ag, Cu, Zn, Pb and U ores from the Alexander shaft from 1947 to 1991; the main Pošepný vein provided up to 95% of production of all the Vrančice deposit (Kopečný, 2012). The Vrančice deposit belongs to the outer part of the Central Bohemian Plutonic Complex and is located in the endocontact with the rocks of the Barrandien volcano-sedimentary complex. The most common rock cropping out in the area is granodiorite, of a type known as the 'rim' type of the Blatná granodiorite (Habásko, 1972). The Vrančice deposit is one of the smaller base-metal and uranium deposits in the outer part of the Příbram ore area.

The old dumps on Vraněč hill are known for the occurrence of >25 minerals (see full list on mindat.org at <https://www.mindat.org/loc-236977.html>). Vésigniéite was described by Paděra and Johan (1957); hedyphane, vanadinite, mottramite, pyromorphite, pseudomalachite, cerussite and iodargyrite were identified by Mrázek and Švihnos (1980). Mrázek and Táborský (1981) found the new mineral čechite, named after Professor František Čech from the Charles University of Prague. The list of minerals from the Vraněč hill was expanded thanks to Mrázek and Švihnos (1982) with brandtite, conicalcite, chervetite, volborthite, langite and cinnabar. Mrázek (1982) further added descloizite and meta-torbernite. Ondruš and Hyršl (1989) described duftite, posnjakite, wulfenite and a mineral belonging to the mixite group, later determined as agardite-(Ce) by Sejkora *et al.* (2008).

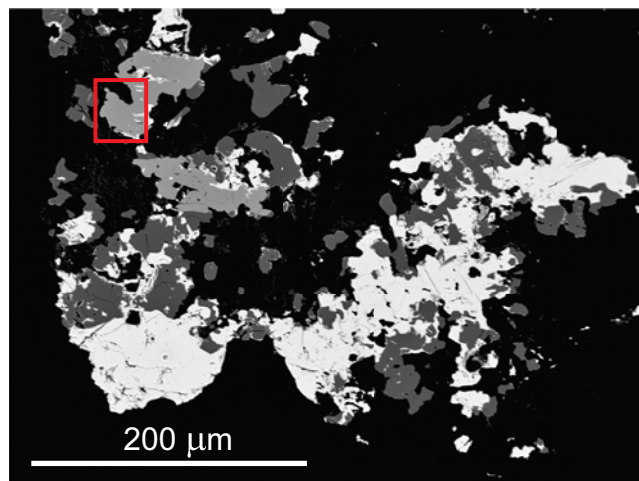
The specimen containing vrančiceite comprises earlier hematite-rich calcite separated distinctly from later milky-white calcite. The earlier strongly hematitised calcite hosts aggregates of hedyphane and Cu-sulfides up to 1 mm in size. The band of later milky-white calcite up to 2.5 cm thick, besides vrančiceite, contains up to 1 cm large fragments of the earlier hematitised calcite strongly intergrown with hedyphane, white or yellowish hedyphane aggregates up to 7 mm in size, cinnabar grains up to 2 mm across, djurleite aggregates up to 5 mm in length, and grains of galena up to 200  $\mu\text{m}$  in size. The crystallisation of vrančiceite is related to a low- $T$  (<100°C) hydrothermal event.

### Physical and optical properties

Vrančiceite forms anhedral grains up to 100  $\mu\text{m}$  in size (Fig. 1). The mineral is black in colour and opaque in transmitted light; it has a metallic lustre. A distinct cleavage in one direction was observed; it is brittle with a conchoidal fracture. The calculated density for the empirical formula ( $Z=2$ ) is 6.652  $\text{g}\cdot\text{cm}^{-3}$ . Mohs hardness is assumed to be 2–3, similar to the associated cinnabar and djurleite. In reflected light, vrančiceite is light grey with a yellowish shade; bireflectance, pleochroism and anisotropy are all weak. Internal reflections were not observed. Reflectance spectra were measured in air with a TIDAS MSP400 spectrophotometer attached to a Leica microscope (100 $\times$  objective) using a WTiC (Zeiss no. 370) standard, with a square sample measurement field of *ca.* 4  $\times$  4  $\mu\text{m}$ . The results for the 400–700 nm range are given in Table 1 and plotted in Fig. 2.

### Chemical composition

Chemical analyses were performed using a Cameca SX100 electron microprobe operating in wavelength-dispersive mode



**Figure 1.** Back-scattered electron image of the holotype material (catalogue number P1P 42/2022). Vrančiceite is medium grey, whereas djurleite is dark grey and light grey are cinnabar and galena. The red box indicates the area where the grain used for single-crystal X-ray diffraction was extracted.

(20 kV, 20 nA and 1  $\mu\text{m}$  beam size). The following standards and X-ray lines were used to minimise line overlaps: Ag ( $\text{AgL}\alpha$ ), Bi ( $\text{BiL}\alpha$ ),  $\text{Bi}_2\text{Se}_3$  ( $\text{SeL}\beta$ ), Cd ( $\text{CdL}\alpha$ ), chalcopyrite ( $\text{CuK}\alpha$ ,  $\text{FeK}\alpha$  and  $\text{SK}\alpha$ ),  $\text{FeAsS}$  ( $\text{AsK}\beta$ ),  $\text{HgS}$  ( $\text{HgL}\alpha$ ),  $\text{NaCl}$  ( $\text{ClK}\alpha$ ),  $\text{PbS}$  ( $\text{PbM}\alpha$ ),  $\text{Sb}_2\text{S}_3$  ( $\text{SbL}\beta$ ), Sn ( $\text{SnL}\beta$ ) and  $\text{ZnS}$  ( $\text{ZnK}\alpha$ ). Peak counting times were 20 s for all elements, and 10 s for each background. Arsenic, Cd, Cl, Fe, Pb, Se, Sn and Zn were all found to be below the detection limits (0.02–0.05 wt.%). Raw intensities were converted to the concentrations of elements using the automatic 'PAP' (Pouchou and Pichoir, 1985) matrix-correction procedure.

Analytical data for vrančiceite (6 analyses) are given in Table 2. On the basis of  $\Sigma\text{Me} = 13$  atoms per formula unit the empirical chemical formula is  $\text{Cu}_{10.11(4)}\text{Ag}_{0.01(1)}\text{Hg}_{2.87(4)}\text{Sb}_{0.01(1)}\text{Bi}_{0.01(1)}\text{S}_{7.99(8)}$ . The ideal formula is  $\text{Cu}_{10}\text{Hg}_3\text{S}_8$ , which requires Cu 42.54, Hg 40.29 and S 17.17, a total of 100.00 wt.%.

### X-ray diffraction data

A short prismatic fragment of vrančiceite, 60  $\times$  40  $\times$  30  $\mu\text{m}$  in size, extracted from the polished section analysed using an electron microprobe (Fig. 1), was mounted on a glass fibre and examined with a Bruker D8 Venture single-crystal diffractometer equipped with an air-cooled Photon III area detector and microfocus

**Table 1.** Reflectance values (%) for vrančiceite.\*

$R_{\text{max}}$	$R_{\text{min}}$	$\lambda$ (nm)	$R_{\text{max}}$	$R_{\text{min}}$	$\lambda$ (nm)
33.0	30.4	400	33.7	30.4	560
33.2	30.9	420	33.3	30.2	580
33.2	31.1	440	<b>33.1</b>	<b>30.0</b>	<b>589</b>
33.4	31.3	460	33.0	29.9	600
<b>33.6</b>	<b>31.2</b>	<b>470</b>	32.5	29.6	620
33.7	31.1	480	32.2	29.3	640
34.0	31.1	500	<b>32.1</b>	<b>29.1</b>	<b>650</b>
34.0	30.9	520	31.9	29.0	660
33.9	30.7	540	31.8	28.8	680
<b>33.9</b>	<b>30.6</b>	<b>546</b>	31.6	28.5	700

\*The reference wavelengths required by the Commission on Ore Mineralogy (COM) are given in bold.

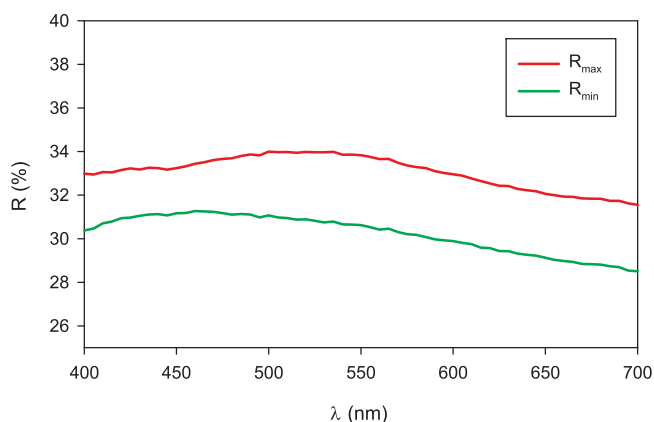


Figure 2. Reflectance curve for vrančiceite.

MoK $\alpha$  radiation (Centro per l'Integrazione della Strumentazione Scientifica dell'Università di Pisa, University of Pisa). The detector-to-crystal distance was 38 mm. Data were collected using  $\omega$  and  $\varphi$  scan modes, in  $0.5^\circ$  slices, with an exposure time of 15 s per frame. A total of 3462 frames were collected and they were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for Lorentz-polarisation, absorption and background. Unit-cell parameters, refined on the basis of the XYZ centroids of 9884 reflections above  $20\sigma(I)$  with  $5.30 < 2\theta < 62.06^\circ$ , are  $a = 7.9681(2)$ ,  $b = 9.7452(3)$ ,  $c = 10.0710(3)$  Å,  $\alpha = 77.759(1)$ ,  $\beta = 76.990(1)$ ,  $\gamma = 79.422(1)^\circ$  and  $V = 737.01(4)$  Å<sup>3</sup>. The  $a:b:c$  ratio calculated from unit-cell parameters is 0.8176:1:1.0335. The statistical test on the distribution of the  $|E|$  values ( $|E^2 - 1| = 0.931$ ) is in accord with the centric nature of vrančiceite. The crystal structure of vrančiceite was then solved in the space group  $P\bar{1}$  using *ShelxTL* and refined using *Shelxl-2018* (Sheldrick, 2015). Three independent Hg sites, eleven Cu positions, and eight S sites were located. Neutral-scattering curves for Hg, Cu and S sites were taken from the *International Tables for Crystallography* (Wilson, 1992). After several cycles of isotropic refinement, the  $R_1$  factor converged to 0.0993, suggesting the correctness of the structural model. All sites were found fully occupied and their site occupancies were then fixed to 1. At the last stage, the anisotropic structural model converged to  $R = 0.0262$  for 4212 reflections with  $F_o > 4\sigma(F_o)$  and 193 refined parameters. Details of data collection and refinement are given in Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters are reported in Table 4. Table 5 reports selected bond distances, whereas bond-valence sums (BVS), calculated according to Brese and O'Keeffe (1991), are shown in Table 6. Anisotropic displacement

Table 2. Electron-microprobe analyses and chemical data (wt.%) for vrančiceite ( $n = 6$ ).

Constituent	Mean	Range	S.D. ( $\sigma$ )
Cu	43.87	43.31–44.73	0.53
Ag	0.06	0.00–0.08	0.03
Hg	39.24	38.70–39.71	0.33
Sb	0.05	0.00–0.17	0.07
Bi	0.09	0.00–0.35	0.15
S	17.49	17.38–17.60	0.10
<b>Total</b>	<b>100.80</b>	<b>100.14–101.66</b>	<b>0.57</b>

S.D. – standard deviation

Table 3. Summary of data collection conditions and refinement parameters for vrančiceite.

Crystal data	
Chemical formula	Cu <sub>10</sub> Hg <sub>3</sub> S <sub>8</sub>
Crystal size (mm)	0.060 × 0.040 × 0.030
Cell setting, space group	Triclinic, $P\bar{1}$
$a$ (Å)	7.9681(2)
$b$ (Å)	9.7452(3)
$c$ (Å)	10.0710(3)
$\alpha$ (°)	77.759(1)
$\beta$ (°)	76.990(1)
$\gamma$ (°)	79.422(1)
$V$ (Å <sup>3</sup> )	737.01(4)
$Z$	2
Data collection	
Radiation, wavelength (Å)	MoK $\alpha$ , $\lambda = 0.71073$
Temperature (K)	293(2)
$2\theta_{\max}$ (°)	62.07
Measured reflections	48661
Unique reflections	4709
Reflections with $F_o > 4\sigma(F_o)$	4212
$R_{\text{int}}$	0.0319
$R\sigma$	0.0178
Range of $h, k, l$	$-11 \leq h \leq 11$ , $-14 \leq k \leq 14$ , $-14 \leq l \leq 14$
Refinement	
$R$ [ $F_o > 4\sigma(F_o)$ ]	0.0262
$R$ (all data)	0.0298
$wR$ (on $F_o^2$ )*	0.0702
Goof	1.033
Number of least-squares parameters	193
Maximum and minimum residual peak ( $e^- \text{Å}^{-3}$ )	1.85 [at 0.68 Å from Hg(1)] -3.04 [at 0.74 Å from Cu(1)]

$$*w = 1/[\sigma^2(F_o^2) + (0.0318P)^2 + 8.6260P], \text{ where } P = (F_o^2 + 2F_c^2)/3$$

parameters are reported in the Crystallographic Information File, deposited with the Principal Editor of *Mineralogical Magazine* and available as Supplementary material (see below).

Powder X-ray diffraction data could not be collected, due to the paucity of available material. Consequently, powder X-ray

Table 4. Sites, Wyckoff position (Wyc.), fractional atom coordinates, equivalent isotropic displacement parameters (Å<sup>2</sup>) for vrančiceite.

Site	Wyc.	$x/a$	$y/b$	$z/c$	$U_{\text{eq}}$
Hg(1)	$2i$	-0.01484(3)	0.38477(2)	0.87184(2)	0.02097(6)
Hg(2)	$2i$	0.24807(3)	0.00596(2)	0.49653(2)	0.02135(6)
Hg(3)	$2i$	0.51318(3)	0.61430(2)	0.11041(3)	0.02388(6)
Cu(1)	$2i$	0.69958(17)	0.50606(12)	0.36142(11)	0.0495(3)
Cu(2)	$2i$	0.18788(18)	0.45409(11)	0.42279(12)	0.0487(3)
Cu(3)	$2i$	-0.00055(12)	0.72765(9)	0.66093(9)	0.02944(17)
Cu(4)	$2i$	0.75299(12)	0.81030(11)	-0.13475(9)	0.03243(19)
Cu(5)	$2i$	0.50479(12)	0.28640(10)	0.33574(9)	0.03009(17)
Cu(6)	$2i$	0.25501(12)	0.83393(10)	-0.14661(9)	0.03341(19)
Cu(7)	$1a$	0	0	0	0.0394(3)
Cu(8)	$2i$	0.13060(11)	0.86707(9)	0.25393(8)	0.02784(17)
Cu(9)	$2i$	0.63523(11)	0.88450(9)	0.24776(8)	0.02969(18)
Cu(10)	$2i$	0.37198(11)	0.69745(9)	0.43045(9)	0.02997(17)
Cu(11)	$1d$	$\frac{1}{2}$	0	0	0.0415(3)
S(1)	$2i$	0.1006(2)	0.68642(15)	0.44016(15)	0.0208(3)
S(2)	$2i$	-0.20618(17)	0.58800(14)	0.79837(14)	0.0166(2)
S(3)	$2i$	0.06145(17)	0.93199(14)	-0.28885(13)	0.0154(2)
S(4)	$2i$	0.43569(17)	0.07783(14)	0.28151(13)	0.0154(2)
S(5)	$2i$	0.83236(16)	0.82785(13)	0.06040(13)	0.0144(2)
S(6)	$2i$	0.63877(19)	0.70864(15)	0.43936(14)	0.0198(2)
S(7)	$2i$	0.70782(17)	0.40946(14)	0.18206(14)	0.0170(2)
S(8)	$2i$	0.32828(16)	0.83059(13)	0.05951(13)	0.0146(2)

**Table 5.** Selected Cu–S and Hg–S distances (in Å) for vrančiceite.

Hg(1)–S(2)	2.3606(13)	Cu(1)–S(7)	2.1905(16)	Cu(5)–S(7)	2.2910(16)	Cu(8)–S(8)	2.2676(15)
Hg(1)–S(5)	2.3694(13)	Cu(1)–S(6)	2.2097(17)	Cu(5)–S(6)	2.3023(16)	Cu(8)–S(1)	2.2862(16)
Average	2.3650	Average	2.2001	Cu(5)–S(4)	2.3979(16)	Cu(8)–S(3)	2.2912(15)
Hg(1)–S(7)	3.3230(14)	Cu(1)–S(1)	2.965(2)	Average	2.3304	Average	2.2817
Hg(1)–S(8)	3.4134(13)	Cu(1)–S(6)	3.6778(18)	Cu(5)–S(2)	2.9429(16)	Cu(8)–S(5)	3.5110(16)
Hg(1)–S(7)	3.4231(14)					Cu(8)–S(4)	3.5474(16)
Hg(1)–S(1)	3.5897(15)	Cu(2)–S(1)	2.2749(17)	Cu(6)–S(8)	2.2717(15)		
		Cu(2)–S(2)	2.3172(17)	Cu(6)–S(3)	2.2841(15)	Cu(9)–S(5)	2.2631(15)
Hg(2)–S(3)	2.3850(13)	Cu(2)–S(6)	2.3400(17)	Cu(6)–S(7)	2.4280(15)	Cu(9)–S(4)	2.2631(15)
Hg(2)–S(4)	2.3872(13)	Average	2.3107	Average	2.3279	Cu(9)–S(6)	2.2947(15)
Average	2.3861	Cu(2)–S(1)	2.827(2)	Cu(6)–S(4)	2.7267(16)	Average	2.2736
Hg(2)–S(6)	3.3030(15)			Cu(6)–S(5)	3.4930(16)	Cu(9)–S(3)	3.4003(16)
Hg(2)–S(3)	3.4730(13)	Cu(3)–S(1)	2.2821(16)	Cu(6)–S(5)	3.5426(16)	Cu(9)–S(8)	3.5825(16)
Hg(2)–S(4)	3.6083(13)	Cu(3)–S(3)	2.3164(16)				
		Cu(3)–S(2)	2.3348(16)	Cu(7)–S(5)	2.2344(13)	Cu(10)–S(1)	2.1639(17)
Hg(3)–S(8)	2.3702(13)	Average	2.3111	Cu(7)–S(5)	2.2344(13)	Cu(10)–S(6)	2.1711(17)
Hg(3)–S(7)	2.3806(13)	Cu(3)–S(7)	3.0572(17)	Average	2.2344	Average	2.1675
Average	2.3650			Cu(7)–S(8)	2.9373(13)	Cu(10)–S(7)	3.7576(16)
Hg(3)–S(2)	3.2719(13)	Cu(4)–S(5)	2.2435(15)	Cu(7)–S(8)	2.9373(13)		
Hg(3)–S(2)	3.4510(14)	Cu(4)–S(4)	2.3128(16)	Cu(7)–S(3)	3.0329(13)	Cu(11)–S(8)	2.2355(13)
Hg(3)–S(5)	3.4606(13)	Cu(4)–S(2)	2.3482(16)	Cu(7)–S(3)	3.0329(13)	Cu(11)–S(8)	2.2355(13)
		Average	2.3015			Average	2.2355(13)
		Cu(4)–S(3)	2.9031(16)			Cu(11)–S(5)	2.9765(13)
		Cu(4)–S(8)	3.5009(16)			Cu(11)–S(5)	2.9765(13)
		Cu(4)–S(8)	3.6486(16)			Cu(11)–S(4)	2.9984(13)
						Cu(11)–S(4)	2.9984(13)

diffraction data, given in Table 7, were calculated using the software *PowderCell* 2.3 (Kraus and Nolze, 1996) on the basis of the structural model given in Tables 3 and 4.

### Crystal structure of vrančiceite

Vrančiceite displays a new crystal structure type among Cu–Hg chalcogenides. It can be described as  $\{0\bar{1}1\}$  Cu–S layers, connected through  $\text{CuS}_3$  polyhedra, giving rise to a three-dimensional framework with channels running along the **a** axis and hosting linearly coordinated Hg atoms (Fig. 3). In addition to Cu–S and Hg–S bonds, there are some short Cu–Cu contacts, probably playing a role in the coordination environments of Cu atoms, as observed in other Cu phases, e.g. in gortdrumite (Bindi *et al.*, 2018).

In the crystal structure of vrančiceite there are 14 cation sites. Among these, the Cu atoms are hosted at 11 symmetry-independent positions, showing variable coordinations. Considering the shortest (= the strongest) Cu–S bonds, Cu coordinations can be described as quasi-linear or triangular. Four Cu atoms, Cu(1), Cu(7), Cu(10) and Cu(11) sites, have quasi-linear coordination. Their average bond distances range between 2.17 Å and 2.24 Å, whereas S–Cu–S angles vary between  $144.77(8)^\circ$  and  $180^\circ$ . These bond distances can be compared with those observed in linearly-coordinated Cu atoms in balkanite (2.197 Å – Biagioni and Bindi, 2017) as well as in other Cu sulfides, e.g. djurleite (2.19 Å – Evans, 1979), and pearceite–polybasite-series minerals (2.16–2.17 Å; Bindi *et al.*, 2006; Evain *et al.*, 2006). Bond-valence sums at these Cu sites range between 0.72 and 0.87 valence units (vu). Taking into account longer Cu–S contacts, the BVS at Cu sites increases, varying between 0.86 and 0.92 vu. Seven triangularly coordinated Cu sites were found in the crystal structure of vrančiceite: Cu(2), Cu(3), Cu(4), Cu(5), Cu(6), Cu(8) and Cu(9). Average bond distances are in the range 2.27–2.33 Å, with bond-valence sums between 0.84 and 0.99 vu. These average bond distances for triangularly coordinated Cu atoms can be compared with those observed in other

Cu sulfides, e.g. in some tetrahedrite-group minerals (2.259 Å – Wuensch, 1964; 2.262 Å – Biagioni *et al.*, 2020; 2.251 Å – Biagioni *et al.*, 2022). In gortdrumite, Bindi *et al.* (2018) reported longer Cu–S bond distances (2.38 Å), whereas three-fold coordinated Cu atoms in balkanite have average distances similar to those observed in vrančiceite, varying between 2.26 and 2.32 Å (Biagioni and Bindi, 2017).

Several short Cu–Cu contacts are also present, for both two- and three-fold coordinated Cu atoms. All Cu sites, with the exception of Cu(8), Cu(9) and Cu(11), display one or two Cu–Cu distances shorter than 2.75 Å, with some short values such as that shown by the pair Cu(1)–Cu(10), i.e. 2.6012(15) Å, slightly longer than that observed in metallic copper, i.e. 2.55 Å (Suh *et al.*, 1988). These Cu–Cu contacts are longer than those observed in balkanite (Biagioni and Bindi, 2017) and similar to some Cu–Cu distances reported by Bindi *et al.* (2018) in gortdrumite. Also the Cu–Hg selenide brodtkorbite shows short Cu–Cu contacts, ranging between 2.535 and 2.670 Å (Sejkora *et al.*, 2017).

The three independent Hg sites have linear coordination, with average  $\langle\text{Hg–S}\rangle$  distances ranging between 2.36 and 2.39 Å, and S–Hg–S angles varying between  $173.07(5)^\circ$  and  $179.49(4)^\circ$ . These distances are comparable with those observed in other minerals characterised by linearly-coordinated Hg, e.g. cinnabar (2.368 Å – Auvray and Genet, 1973), imiterite (2.376 Å – Guillou *et al.*, 1985), rouxelite (2.381 Å – Orlandi *et al.*, 2005), marrucciite (2.361 and 2.386 Å for the two independent Hg1 and Hg2 sites – Orlandi *et al.*, 2007), fettelite (2.403 and 2.393 Å for the two independent Hg1 and Hg2 sites – Bindi *et al.*, 2009), balkanite (2.366 Å – Biagioni and Bindi, 2017), and gortdrumite (2.386 Å, as average of five Hg sites – Bindi *et al.*, 2018). Longer Hg–S bonds ( $> 3.25$  Å) complete the coordination environments of Hg atoms. Taking into account Hg–S distances shorter than 3.65 Å, Hg(1) has a 2 + 4 coordination, whereas Hg(2) and Hg(3) display a 2 + 3 coordination. Considering the long (= weak) bonds, the bond-valence sums at the Hg sites range between 1.81 and 1.98 vu. It is worth noting that these weak Hg–S bonds are longer



**Table 6.** Bond valence (in valence units) in vrančiceite.

Site	S(1)	S(2)	S(3)	S(4)	S(5)	S(6)	S(7)	S(8)	$\Sigma$ cations	Expected
Hg(1)	0.03	0.90			0.88		0.07 0.05	0.05	1.98	2.00
Hg(2)			0.84 0.04	0.83 0.03		0.07			1.81	2.00
Hg(3)		0.08 0.05			0.05		0.85	0.87	1.90	2.00
Cu(1)	0.05					0.39 0.01	0.41		0.86	1.00
Cu(2)	0.33 0.07	0.29				0.27			0.96	1.00
Cu(3)	0.32	0.28	0.29				0.04		0.93	1.00
Cu(4)		0.27	0.06	0.29	0.35			0.01 0.01	0.99	1.00
Cu(5)		0.05		0.23		0.30	0.31		0.89	1.00
Cu(6)			0.32	0.10	0.01 0.01		0.22	0.33	0.99	1.00
Cu(7)			$2x \rightarrow 0.04$		$2x \rightarrow 0.36$			$2x \rightarrow 0.05$	0.90	1.00
Cu(8)	0.32		0.31	0.01	0.01			0.33	0.98	1.00
Cu(9)			0.02	0.34	0.34	0.31		0.01	1.02	1.00
Cu(10)	0.44					0.43	0.01		0.88	1.00
Cu(11)				$2x \rightarrow 0.05$	$2x \rightarrow 0.05$			$2x \rightarrow 0.36$	0.92	1.00
$\Sigma$ anions	1.55	1.92	1.92	1.88	2.06	1.78	1.96	2.02		
Expected	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00		

than some Hg–Cu contacts, showing distances in the range 3.10–3.20 Å.

Anion sites are fully occupied by S and are four-fold coordinated, with additional longer Cu–S or Hg–S bonds. Bond-valence sums are in the range 1.55–2.06 vu.

**Table 7.** Calculated powder X-ray diffraction data for vrančiceite.\*

$l_{\text{calc}}$	$d_{\text{calc}}$	$h k l$	$l_{\text{calc}}$	$d_{\text{calc}}$	$h k l$
10	7.440	0 1 1	32	2.623	2 3 0
41	6.214	0 $\bar{1}$ 1	17	2.471	2 $\bar{1}$ 3
11	4.713	0 2 0	20	2.453	2 $\bar{2}$ 2
44	4.646	0 1 2	37	2.445	0 1 4
32	4.569	0 2 1	30	2.390	0 4 1
11	3.834	2 0 1	11	2.388	2 3 3
20	3.750	2 1 0	39	2.244	0 $\bar{1}$ 4
11	3.720	0 2 2	22	2.224	$\bar{2}$ 3 1
36	3.393	2 $\bar{1}$ 0	21	2.219	$\bar{2}$ 1 3
<b>76</b>	<b>3.354</b>	<b><math>\bar{2}</math> 0 1</b>	21	2.201	0 4 1
15	3.227	0 1 3	14	2.093	2 3 4
15	3.224	$\bar{2}$ $\bar{1}$ 1	28	1.962	4 1 2
22	3.218	0 0 3	17	1.921	4 0 0
15	3.142	0 3 0	10	1.892	2 $\bar{4}$ 0
<b>68</b>	<b>3.111</b>	<b>2 2 2</b>	10	1.886	$\bar{2}$ 0 4
60	3.107	0 2 2	11	1.794	0 3 5
43	2.927	2 $\bar{1}$ 2	17	1.791	0 5 1
52	2.910	0 2 3	13	1.770	0 5 3
63	2.878	0 3 2	15	1.761	2 $\bar{1}$ 5
25	2.842	0 3 1	12	1.754	4 3 0
<b>100</b>	<b>2.833</b>	<b>2 1 3</b>	12	1.752	$\bar{4}$ 1 1
59	2.817	$\bar{2}$ 2 1	11	1.689	2 5 1
11	2.789	2 $\bar{2}$ 0	16	1.681	2 4 5
14	2.743	2 0 3	15	1.657	4 2 2
<b>93</b>	<b>2.733</b>	<b>2 3 1</b>	12	1.613	0 2 6
<b>76</b>	<b>2.705</b>	<b>2 <math>\bar{2}</math> 1</b>	22	1.612	$\bar{4}$ 2 2
17	2.655	$\bar{2}$ 2 1	11	1.555	4 4 4
<b>71</b>	<b>2.647</b>	<b><math>\bar{2}</math> <math>\bar{1}</math> 2</b>	12	1.554	0 4 4
20	2.646	$\bar{2}$ 1 2	10	1.493	4 5 3

\*Intensity and  $d_{\text{hkl}}$  (in Å) were calculated using the software *PowderCell*2.3 (Kraus and Nolze, 1996) on the basis of the structural data given in Tables 3 and 4. Only reflections with  $I_{\text{rel.}} \geq 10$  are listed. The six strongest reflections are given in bold.

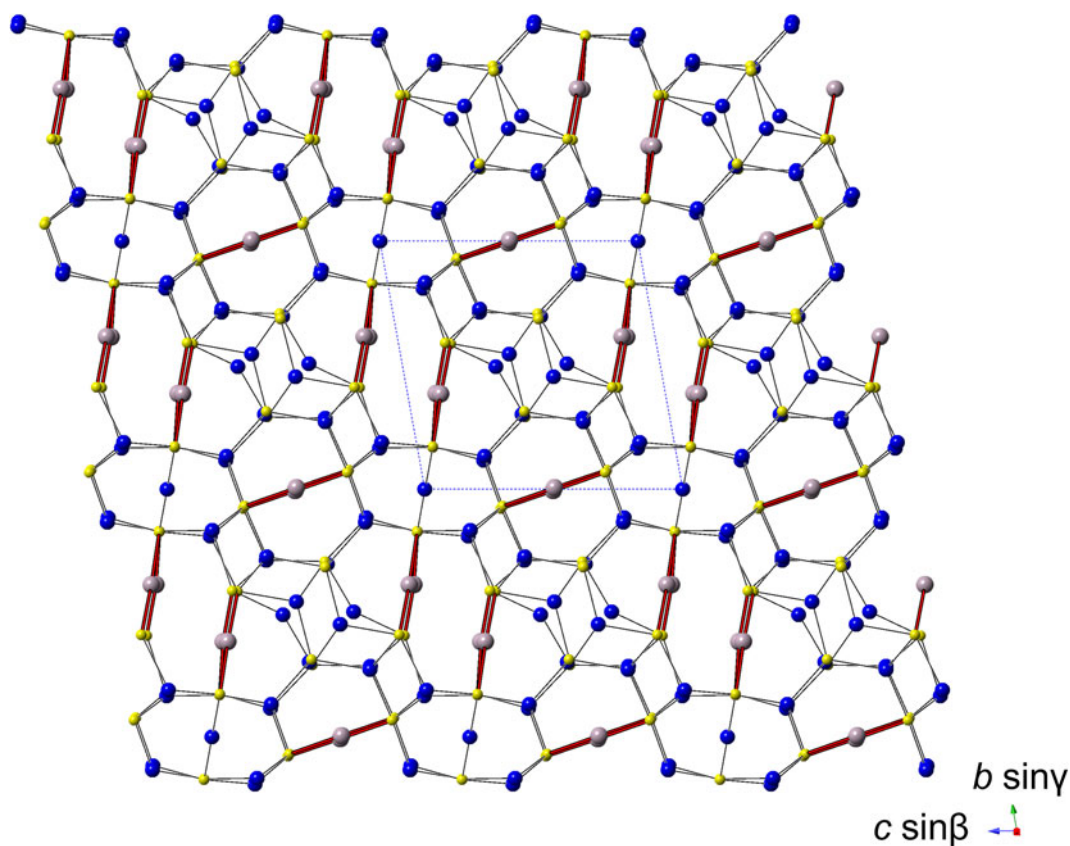
The occurrence of several metal–metal contacts suggests that vrančiceite could be considered as a peculiar sulfide having some features typical of intermetallic compounds, as noted for gortdrumite by Bindi *et al.* (2018). Notwithstanding, the bond-valence considerations seem to be applicable and the results of the bond-valence balance are in reasonable agreement with the expected values (Table 6).

## Discussion

### Vrančiceite and related Cu–Hg sulfides

Vrančiceite is a new member of the Cu–Hg–S system. Ollitrault-Fichet *et al.* (1984) examined the phase diagram of this system but found nothing similar to vrančiceite. They found a ternary phase with composition  $\text{Cu}_{0.42}\text{Hg}_{0.18}\text{S}_{0.39}$  that was only stable at high temperature. The absence of the synthetic analogue of vrančiceite in the experiments of Ollitrault-Fichet *et al.* (1984) suggests that it could be formed at low temperatures.

Among natural Cu–Hg–S phases, ternary compounds are represented by two species: the inadequately described ‘bayankhanite’, from the fluorite deposit of Idermeg-Bayan-Khan-Ula, Mongolia (Kuznetsov *et al.*, 1978; Vasil’ev, 1984), and danielsite,  $(\text{Cu}, \text{Ag})_{14}\text{HgS}_8$  (Nickel, 1987; Kato and Nickel, 1988). Three published chemical analyses of the former show a very wide range of Cu and Hg, ranging between 20.9 and 40.9 wt.% and 43 and 59 wt.%, respectively. Among these analyses, one has Cu 40.9, Hg 43.0 and S 17.0 wt.%, close to the composition of vrančiceite (Fig. 4); in addition, the powder X-ray diffraction data of ‘bayankhanite’ are of very low quality, although similar to those of vrančiceite (Vasil’ev, 1984). On the other hand, its optical properties (strong birefractance and anisotropy) are fundamentally different from vrančiceite. In any case, ‘bayankhanite’ was discredited by Burke (2006). Danielsite is poorly characterised, and its actual relationship with balkanite is unclear (Biagionis and Bindi, 2017); as shown in Fig. 4, their composition is very similar.



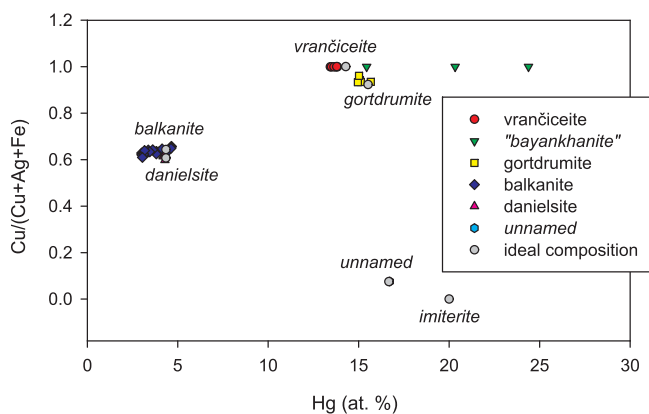
**Figure 3.** Crystal structure of vrančiceite as seen down the *a* axis. Blue, violet and yellow circles are Cu, Hg and S atoms, respectively. Hg–S bonds are shown as thick red lines, whereas thin black lines indicate Cu–S bonds. The unit cell is shown with dashed lines. Drawn using *CrystalMaker*® software.

Vrančiceite has an Hg content (in atom%) and a Cu/(Cu+Ag+Fe) atomic ratio close to that of gortdrumite. Indeed, as discussed in the Introduction, Škácha and Sejkora (2013) first identified vrančiceite as an Fe-free gortdrumite. Their structural relationship deserves further discussion.

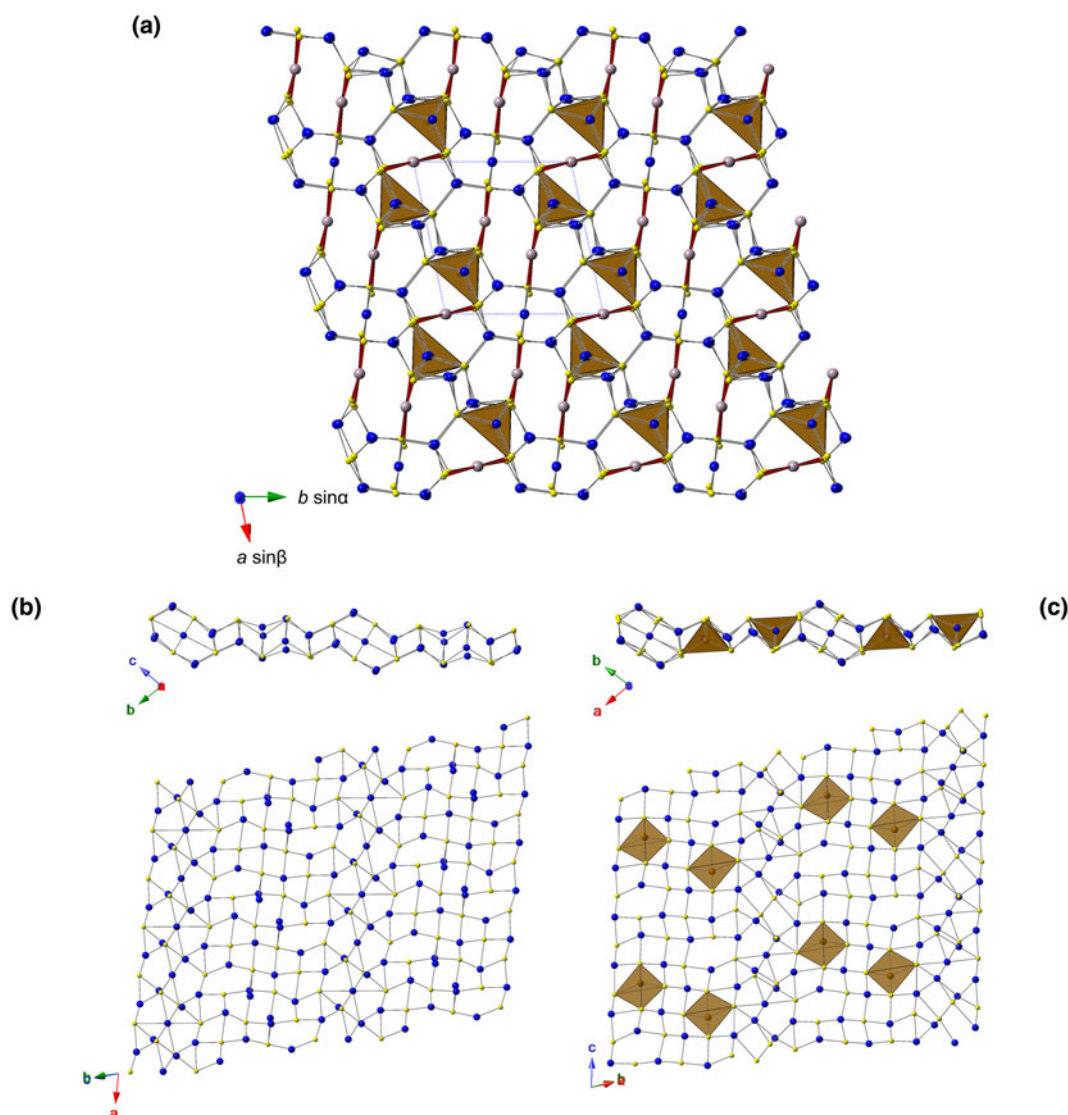
**Relations between vrančiceite and gortdrumite**

The crystal structure of gortdrumite, reported by Bindi *et al.* (2018), can be described as a succession of {110} layers. As in vrančiceite, linearly coordinated Hg atoms are hosted in channels running along the *c* axis (Fig. 5). A comparison between the projections of the crystal structures of vrančiceite and gortdrumite (Figs 3 and 5) reveals a striking similarity in the layer morphology as well as in the directions of Hg–S bonds. Moreover, the two crystal structures can be better compared transforming the axial setting of gortdrumite through the matrix [0 0 1 | 1 0 0 | 0 1 0]. Table 8 compares the unit-cell parameters of these two species. Whereas the transformed *b* and *c* axes of gortdrumite are slightly shorter than that of vrančiceite, the *a* axis of the former is significantly longer than that of the latter, explaining the volume increase observed in gortdrumite ( $\Delta V/V = +46.1\%$ ).

The Cu–(Fe)–S layers of vrančiceite and gortdrumite are compared in Figs 5b and c. Along the channel directions (upper part of Figs 5b and c), the layers can be divided into two portions: the first one is a two-atom-thick zig-zag ribbon, whereas the second one has an elliptical shape. Figure 6 shows the differences between these layers in vrančiceite and gortdrumite. In both minerals, the zig-zag ribbons are six-atoms-wide (Fig. 6a,b); however, their chemical composition is different, with gortdrumite showing the insertion of a  $\text{Cu}_4\text{Fe}_2\text{S}_6$  fragment and the omission of 2 Cu atoms [corresponding to the Cu(1) atom in vrančiceite]. Consequently, the chemistry of the zig-zag ribbons in vrančiceite and gortdrumite is  $\text{Cu}_{14}\text{S}_{12}$  and  $\text{Cu}_{16}\text{Fe}_2\text{S}_{18}$ ,



**Figure 4.** Chemical composition of minerals of the system Cu–Ag–Hg–S in the plot Hg (at.%) vs. Cu/(Cu+Ag+Fe) (at. units). Ideal compositions and published data: vrančiceite  $\text{Cu}_{10}\text{Hg}_3\text{S}_8$  (this paper); discredited ‘bayankhanite’ (Kuznetsov *et al.*, 1978; Vasil’ev, 1984); gortdrumite  $\text{Cu}_{24}\text{Fe}_2\text{Hg}_9\text{S}_{23}$  (Steed, 1983; Bindi *et al.*, 2018); balkanite  $\text{Cu}_9\text{Ag}_5\text{HgS}_8$  (Atanassov and Kirov, 1973; Paar and Chen, 1985; Steiner *et al.*, 2010; Biagioni and Bindi, 2017; Sejkora *et al.*, 2022); danielsite  $(\text{Cu}_{8.5}\text{Ag}_{5.5})_{\Sigma 14}\text{HgS}_8$  (Nickel, 1987; Kato and Nickel, 1988), unnamed  $(\text{Ag}_{7.4}\text{Cu}_{0.6})_{\Sigma 8}\text{Hg}_3(\text{S},\text{Se})_7$  (Paar *et al.*, 2004); and imiterite  $\text{Ag}_2\text{HgS}_2$  (Guillou *et al.*, 1985).



**Figure 5.** (a) Crystal structure of gortdrumite as seen down the *c* axis. Blue, violet and yellow circles are Cu, Hg and S atoms, respectively; Fe-centred tetrahedra are shown in brown. Hg–S bonds are shown as thick red lines, whereas thin black lines indicate Cu–S bonds. (b) The {011} Cu–S layer in vrančiceite, as seen down *a* and perpendicular to the layer. (c) The {110} Cu–Fe–S layer in gortdrumite, as seen down *c* and perpendicular to the layer. Drawn using *CrystalMaker*® software.

respectively. The remaining portion of the layers has a composition of  $\text{Cu}_6\text{S}_4$  in vrančiceite and  $\text{Cu}_8\text{S}_5$  in gortdrumite (Fig. 6c, d). Also in this case, the intercalation of a  $\text{Cu}_2\text{S}$  fragment increases the parameter along the ribbon elongation of gortdrumite. As a whole, the Cu–(Fe)–S layers have a chemical composition of

**Table 8.** Comparison between unit-cell parameters in vrančiceite and gortdrumite.

	vrančiceite	gortdrumite*
<i>a</i> (Å)	7.9681(2)	11.992(5)
<i>b</i> (Å)	9.7452(3)	9.677(4)
<i>c</i> (Å)	10.0710(3)	9.865(5)
$\alpha$ (°)	77.759(1)	76.30(4)
$\beta$ (°)	76.990(1)	77.85(4)
$\gamma$ (°)	79.422(1)	79.42(3)
<i>V</i> (Å <sup>3</sup> )	737.01(4)	1076.5(8)
Unit-cell content	$\text{Cu}_{20}\text{Hg}_6\text{S}_{16}$	$\text{Cu}_{24}\text{FeHg}_9\text{S}_{23}$

\*unit-cell parameters transformed through the matrix  $\begin{bmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix}$ .

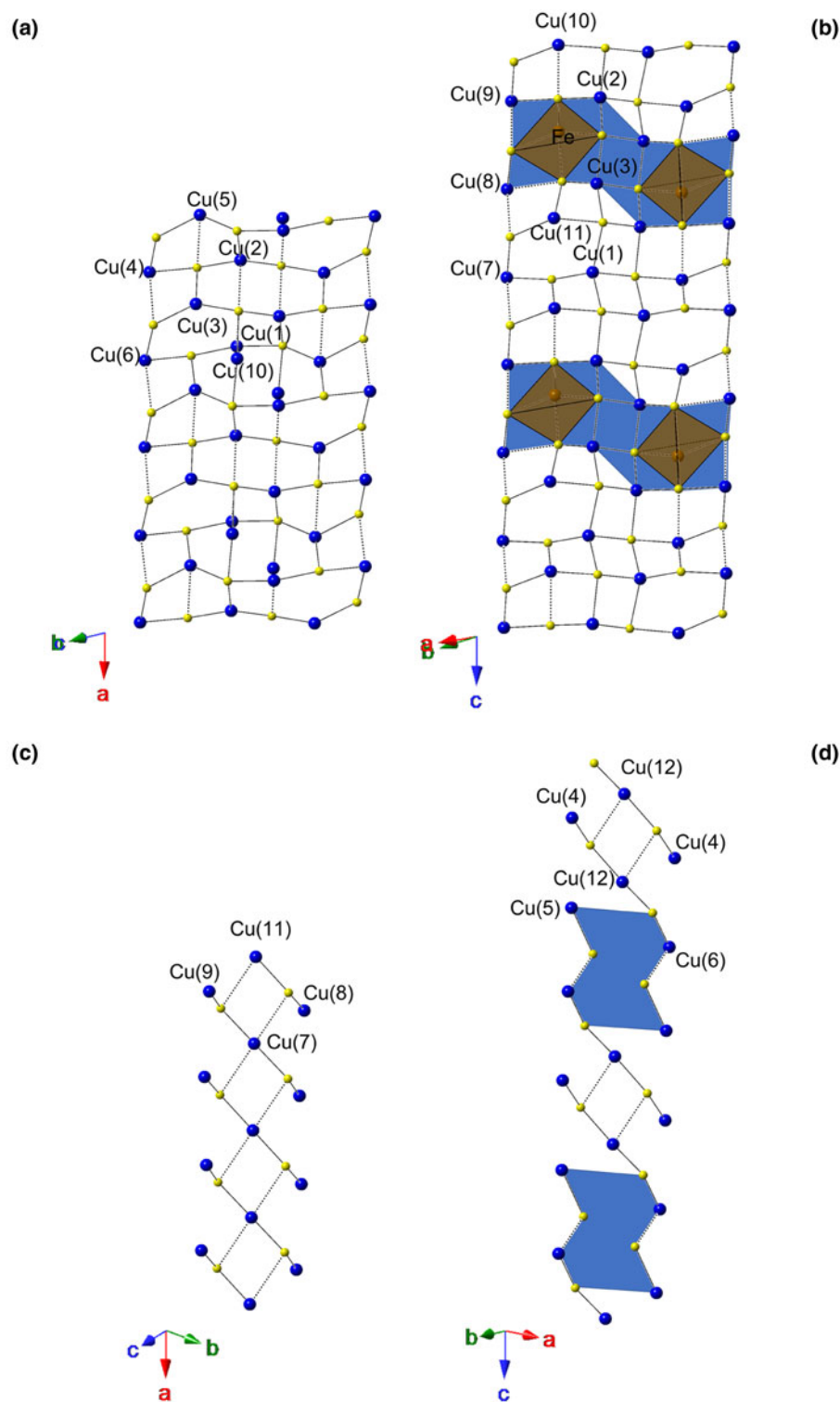
$\text{Cu}_{14}\text{S}_{12} + \text{Cu}_6\text{S}_4 = \text{Cu}_{20}\text{S}_{16}$  in vrančiceite and  $\text{Cu}_{16}\text{Fe}_2\text{S}_{18} + \text{Cu}_8\text{S}_5 = \text{Cu}_{24}\text{Fe}_2\text{S}_{23}$  in gortdrumite.

In both minerals, these layers are decorated, on both sides, by Hg atoms. The increased size of the gortdrumite layers favours the addition of further Hg atoms with respect to vrančiceite. Indeed, three additional Hg atoms occur in the former, having the unit-cell content  $\text{Cu}_{24}\text{Fe}_2\text{Hg}_9\text{S}_{23}$ , compared with the unit-cell content of vrančiceite,  $\text{Cu}_{20}\text{Hg}_6\text{S}_{16}$ .

## Conclusions

Vrančiceite is a new ternary phase in the Cu–Hg–S system. Its discovery and comparison with previously known Cu–Hg chalcogenides confirm the fundamental role of studies devoted to natural mineral assemblages to reveal novel crystal structures so far not obtained in laboratory synthesis experiments (e.g. Ollitrault-Fichet *et al.*, 1984; Bindi *et al.*, 2020).

Vrančiceite is a contracted derivative of gortdrumite, obtained through the omission of a zig-zag Fe-bearing structural fragment.



**Figure 6.** Details of the Cu-(Fe)-S layers in vrančiceite (a, c) and gortdrumite (b, d), showing the insertion of structural fragments in the latter (highlighted in blue). In (a) and (b), the zig-zag ribbons are shown perpendicularly to their layering, whereas in (c) and (d) the remaining portion of the layers are displayed. Drawn using *CrystalMaker*<sup>®</sup> software.

These two minerals can thus be considered a new example of a plesiotypic pair (e.g. Makovicky, 1997; Ferraris *et al.*, 2004). Moreover, this is an additional case showing the role of minor elements in the crystallisation of different mineral species: the occurrence or absence of minor Fe can favour the formation of gortdrumite [Fe/(Fe+Cu+Hg)*at.* ratio = 0.06] or vrančiceite [Fe/(Fe+Cu+Hg)*at.* ratio = 0.00], that consequently reflects the variable geochemistry of hydrothermal environments.

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**Supplementary material.** The supplementary material for this article can be found at <https://doi.org/10.1180/mgm.2023.40>.

**Competing interests.** The authors declare none.

## References

- Atanassov V.A. and Kirov G.N. (1973) Balkanite,  $\text{Cu}_9\text{Ag}_5\text{HgS}_8$ , a new mineral from the Sedmochislenitsi mine, Bulgaria. *American Mineralogist*, **58**, 11–15.
- Auvray P and Genet F. (1973) Affinement de la structure cristalline du cinabre  $\alpha$ -HgS. *Bulletin de la Société Française de Minéralogie et de Cristallographie*, **96**, 218–219.
- Biagioni C. and Bindi L. (2017) Ordered distribution of Cu and Ag in the crystal structure of balkanite,  $\text{Cu}_9\text{Ag}_5\text{HgS}_8$ . *European Journal of Mineralogy*, **29**, 279–285.
- Biagioni C., Sejkora J., Musetti S., Velebil D. and Pasero M. (2020) Tetrahedrite-(Hg), a new 'old' member of the tetrahedrite group. *Mineralogical Magazine*, **84**, 584–592.
- Biagioni C., Sejkora J., Musetti S., Makovicky E., Pagano R., Pasero M. and Dolníček Z. (2022) Stibiofieldite,  $\text{Cu}_{12}(\text{Sb}_2\text{Te}_2)\text{S}_{13}$ , a new tetrahedrite-group mineral. *Mineralogical Magazine*, **86**, 168–175.
- Bindi L., Evain M. and Menchetti S. (2006) Temperature dependence of the silver distribution in the crystal structure of natural pearceite,  $(\text{Ag}, \text{Cu})_{16}(\text{As}, \text{Sb})_2\text{S}_{11}$ . *Acta Crystallographica*, **B62**, 212–219.
- Bindi L., Keutsch F.N., Francis C.A. and Menchetti S. (2009) Fettelite,  $[\text{Ag}_6\text{As}_2\text{S}_7][\text{Ag}_{10}\text{HgAs}_2\text{S}_8]$  from Chanarcillo, Chile: Crystal structure, pseudosymmetry, twinning, and revised chemical formula. *American Mineralogist*, **94**, 609–615.
- Bindi L., Paar W.H. and Leblhuber P. (2018) Gortdrumite,  $\text{Cu}_{24}\text{Fe}_2\text{Hg}_9\text{S}_{23}$ , from Leogang, Salzburg, Austria: crystal structure and revision of the chemical formula. *Mineralogical Magazine*, **82**, 853–861.
- Bindi L., Nespolo M., Krivovichev S.V., Chapuis G. and Biagioni C. (2020) Producing highly complicated materials. Nature does it better. *Reports on Progress in Physics*, **83**, 106501.
- Brese N.E. and O'Keeffe M. (1991) Bond-valence parameters for solids. *Acta Crystallographica*, **B47**, 192–197.
- Burke E.A.J. (2006) A mass discreditation of GQN minerals. *The Canadian Mineralogist*, **44**, 1557–1560.
- Evain M., Bindi L. and Menchetti S. (2006) Structural complexity in minerals: twinning, polytypism and disorder in the crystal structure of polybasite,  $(\text{Ag}, \text{Cu})_{16}(\text{Sb}, \text{As})_2\text{S}_{11}$ . *Acta Crystallographica*, **B62**, 447–456.
- Evans H.T. (1979) The crystal structure of low chalcocite and djurleite. *Zeitschrift für Kristallographie*, **150**, 299–320.
- Ferraris G., Makovicky E. and Merlino S. (2004) *Crystallography of Modular Materials*. Oxford University Press, New York, 370 p.
- Guillou J.J., Montheil J., Picot P., Pillard F., Protas J. and Samama J.C. (1985) L'imitérite,  $\text{Ag}_2\text{HgS}_2$ , nouvelle espèce minérale; propriétés et structure cristalline. *Bulletin de Minéralogie*, **108**, 457–464.
- Habásko J. (1972) *Geological Project of the Milín Exploration Shaft*. Unpublished report, DIAMO SUL [in Czech].
- Kato A. and Nickel E.H. (1988) Possible unit cell for danielsite. *American Mineralogist*, **73**, 187–188.
- Kopečný P. (2012) *The Base-Metal Deposit Vrančice – Radětice*. Unpublished report, DIAMO, XVII/ 8, 4 [in Czech].
- Kraus W. and Nolze G. (1996) POWDER CELL – a program for the representation and manipulation of crystal structures and calculation of the resulting X-ray powder patterns. *Journal of Applied Crystallography*, **29**, 301–303.
- Kuznetsov V.A., Obolenskiy A.A., Vasil'ev V.I. and Borisenko A.C. (1978) The mercury ores of Mongolia. Pp. 5–26 in: *Geology and Genesis of Rare-Metallic and Polymetallic Deposits of Siberia*. Transactions of the Institute of Geology and Geophysics, Siberian Branch, Academy of Sciences of the USSR (Novosibirsk), 404 [in Russian].
- Makovicky E. (1997) Modular crystal chemistry of sulphosalts and other complex sulphides. *EMU Notes in Mineralogy*, **1**, 237–271.
- Mrázek Z. (1982) Preliminary report on mineralogical findings at the Pošepný vein in Vrančice. *Vlastivědný sborník Podbrdská*, **22**, 79–86 [in Czech].
- Mrázek Z. and Švihnos I. (1980) New minerals from Vrančice. *Časopis pro mineralogii a geologii*, **25**, 95–96 [in Czech].
- Mrázek Z. and Švihnos I. (1982) New minerals from Vrančice II. *Časopis pro mineralogii a geologii*, **27**, 206 [in Czech].
- Mrázek Z. and Táborský Z. (1981) Čechite,  $\text{Pb}(\text{Fe}^{+2}, \text{Mn}^{+2})(\text{VO}_4)(\text{OH})$ , a new mineral of the descloizite-pyrobelenite group. *Neues Jahrbuch für Mineralogie, Monatshefte*, **1981**, 520–528.
- Nickel E.H. (1987) Danielsite: A new sulfide mineral from Western Australia. *American Mineralogist*, **72**, 401–403.
- Ollitrault-Fichet R., Rivet J. and Flahaut J. (1984) Diagramme de phase du système Hg–Cu–S: étude du triangle HgS–Cu<sub>2</sub>S–S. *Journal of the Less Common Metals*, **96**, 49–62.
- Ondruš P. and Hyršl J. (1989) New finds and revision of secondary minerals from Příbram district. *Acta Universitatis Carolinae, Geologica*, **4**, 521–533.
- Orlandi P., Meerschaut A., Moëlo Y., Palvadeau P. and Léone P. (2005) Lead-antimony sulfosalts from Tuscany (Italy). VIII. Rouxelite,  $\text{Cu}_2\text{HgPb}_{22}\text{Sb}_{28}\text{S}_{64}(\text{O}, \text{S})_2$ , a new sulfosalts from Buca della Vena mine, Apuan Alps: definition and crystal structure. *The Canadian Mineralogist*, **43**, 919–933.
- Orlandi P., Moëlo Y., Campostrini I. and Meerschaut A. (2007) Lead-antimony sulfosalts from Tuscany (Italy). IX. Marrucciite,  $\text{Hg}_3\text{Pb}_{16}\text{Sb}_{18}\text{S}_{46}$ , a new sulfosalts from Buca della Vena mine, Apuan Alps: Definition and crystal structure. *European Journal of Mineralogy*, **19**, 267–279.
- Paar W.H. and Chen T.T. (1985) Zur Mineralogie von Cu–Ni–(Co)–Pb–Ag–Hg–Erzen in Revier Schwarzleo bei Leogang, Salzburg, Österreich. *Mitteilungen der Österreichischen Geologischen Gesellschaft*, **78**, 125–148.
- Paar W.H., Topa D., Makovicky E., Sureda R.J., De Brodtkorb M.K., Nickel E.H. and Putz H. (2004) Jaguéite,  $\text{Cu}_2\text{Pd}_3\text{Se}_4$ , a new mineral species from El Chire, La Rioja, Argentina. *The Canadian Mineralogist*, **42**, 1745–1755.
- Paděra K. and Johan Z. (1957) The finds of vanadates in Bohemia. *Časopis pro mineralogii a geologii*, **2**, 187 [in Czech].
- Pouchou J.L., and Pichoir F. (1985) "PAP" ( $\varphi\rho Z$ ) procedure for improved quantitative microanalysis. Pp. 104–106 in: *Microbeam Analysis* (J.T. Armstrong, editor). San Francisco Press, San Francisco.
- Sejkora J., Toegel V. and Pauliš P. (2008) Agardite-(Ce) from supergene zone of Vrančice deposit near Příbram (Czech Republic). *Bulletin mineralogicko-petrologického oddělení Národního muzea v Praze*, **16**, 217–220 [in Czech].
- Sejkora J., Škácha P., Laufek F. and Plášil J. (2017) Brodtkorbite,  $\text{Cu}_2\text{HgSe}_2$ , from Příbram, Czech Republic: crystal structure and description. *European Journal of Mineralogy*, **29**, 663–672.
- Sejkora J., Dolníček Z., Škácha P., Ulmanová J. and Vrtiška L (2022) Unusual mineralization with willemite from the area of the central part of the Příbram uranium and base-metal district (Czech Republic). *Bulletin Mineralogiae Petrologiae*, **30**, 224–242 [in Czech].
- Sejkora J., Biagioni C., Škácha P., and Mauro D. (2023) Vrančiceite, IMA 2022-114. CNMNC Newsletter 72. *Mineralogical Magazine*, **87**, 512–518, <https://doi.org/10.1180/mgm.2023.21>
- Sheldrick G.M. (2015) Crystal structure refinement with SHELXL. *Acta Crystallographica*, **C71**, 3–8.
- Škácha P. and Sejkora J. (2013) The occurrence of cinnabar with microscopic gortdrumite at the Vrančice deposit near Příbram (Czech Republic). *Bulletin mineralogicko-petrologického oddělení Národního muzea v Praze*, **21**, 57–61 [in Czech].
- Steed G.M. (1983) Gortdrumite, a new sulphide mineral containing copper and mercury, from Ireland. *Mineralogical Magazine*, **47**, 35–36.
- Steiner M., Tropper P., Vavtar F., Kaindl R. and Krismer M. (2010) Balkanite from the Cu ore deposit Röhrerbühel, Kitzbühel (N-Tyrol, Austria). *Neues Jahrbuch für Mineralogie, Abhandlungen*, **187**, 207–215.
- Suh I.-K., Ohta H. and Waseda Y. (1988) High-temperature thermal expansion of six metallic elements measured by dilation method and X-ray diffraction. *Journal of Materials Science*, **23**, 757–760.
- Vasil'ev V.I. (1984) New minerals of mercury and mercury-containing deposits and their paragenesis. Pp. 5–21 in: *Geology and Genesis of Rare-Metallic and Polymetallic Deposits of Siberia*. Transactions of the Institute of Geology and Geophysics, Siberian Branch, Academy of Sciences of the USSR (Novosibirsk), **587** [in Russian].
- Wilson A.J.C. (editor) (1992) *International Tables for Crystallography Volume C: Mathematical, Physical and Chemical Tables*. Kluwer Academic Publishers, Dordrecht, The Netherlands.
- Wunsch B.J. (1964) The crystal structure of tetrahedrite,  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ . *Zeitschrift für Kristallographie*, **119**, 437–453.