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Hodrushite—a new sulphosalt

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SUMMARY. Hodrushite, a new sulphosalt of copper and bismuth, was found in the Rosalia ore vein at Banská Hodruša near Banská Štiavnica, Czechoslovakia. It has chemical composition $Cu_{8\cdot12}Bi_{11\cdot54}Fe_{0\cdot29}S_{22}$ (as determined by electron-microprobe method) close to $Cu_8Bi_{12}S_{22}$. Symmetry is monoclinic, space group $A2/m$, lattice constants a 27·21, b 3·93, c 17·58 Å, β 92° 9′, measured density 6·35, calculated density 6·45 g/cm^3. Microhardness 200 kg/mm^2, anisotropic, weak bireflectance, creamy with pinkish tint, maximum reflectivity about 6000 Å. Crystals needle-shaped and striated along [010], colour steel-grey, quickly tarnishing to bronze. Associated with quartz, hematite, and chalcopyrite. Closely related to cuprobismutite.

THIS paper describes a new sulphosalt of copper and bismuth found in ore veins in Banská Hodruša, Czechoslovakia. The metallogenetic region of Banská-Štiavnica–Banská-Hodruša is situated in the southern part of the neovolcanic Kremnica–Štiavnica Ore Mountains representing a part of the Carpathians. Its polymetallic ore deposits of subvolcanic type consist of a vein system developed mostly in propylitized pyroxenic andesites.

The Rosalia vein where the new sulphosalt was found is situated on the west border of the ore district of Banská Štiavnica in the territory of a renowned historical mining centre—the community of Banská Hodruša. Therefore the authors propose the name *hodrushite* for the new mineral.

The mineralization of the Rosalia vein, and that of other veins of Banská Štiavnica ore district, had a pulsatory character and can be divided into six mineralization periods. The second and the fourth represent the main ore-bearing periods of the Rosalia vein. The second period has a polymetallic character with preponderance of galena and sphalerite over chalcopyrite, while the fourth, and younger, period has chalcopyrite prevailing among the ore minerals. Quartz was found in both mineralization periods.

The other periods are non-metalliferous, being composed of quartz in the first period, quartz with very abundant hematite in the third and fifth periods, and quartz, carbonates, and baryte in the sixth period.

A very distinct metal zonation is developed in the district. An upper Au–Ag zone is replaced downwards by a Pb–Zn zone, which is further replaced downwards by a Cu mineralization (Kodĕra, 1963). The Rosalia vein occurs in the deepest zones of the ore district, where it is characterized by a preponderance of Cu ore minerals of which chalcopyrite is by far the most abundant.

Bismuth has been detected only rarely in the ores of the district. It is primarily found in galena where it is isomorphous with Pb; the Bi-content of the galena increases with depth. As galena gradually disappears in the lower zones of the vein the possibility of the formation of distinct Bi minerals increases. Such minerals have actually been found in the Rosalia vein, namely as an isolated occurrence of rézbányite (Kodĕra, 1965) and now by several finds of hodrushite.

Occurrence. Hodrushite was found in the deeper zones of the Rosalia vein, on the 150- and 250-m mining levels. It is present in zones relating to the fourth and fifth mineralization periods in association with quartz, hematite, and locally (mainly in the fourth period) with chalcopyrite and wittichenite (?). As a rule hodrushite forms needle-shaped crystals less than 1 mm in length, irregular grains, or fine-grained aggregates. Occasionally columnar and platy crystals up to 5 mm long are found in quartz–hematite gangue. They are markedly vertically striated and in most cases they represent multiple crystal intergrowths.

Physical properties. Hodrushite has a steel-grey colour with a slight yellowish tint on fresh fractured surfaces. It quickly tarnishes in air, however, to a brownish-bronze colour. The mineral has a metallic lustre, is very brittle, and has no distinct cleavage. The microhardness was determined using a microsclerometer PMT-3 (made in the Soviet Union) with a pressure on the Vickers diamond pyramid of 20 g, exposure time 10 sec. The following microhardness values were determined from 25 measurements: $H_{\max} = 213$ kg/mm², $H_{\min} = 187$ kg/mm², and $H_{av} = 200$ kg/mm², which are equivalent to 38, ·3·5, and 3·7 on Mohs's hardness scale. These values for hodrushit are very similar to those determined on emplectite and wittichenite by Young and Millman (1964).

A portion of hand-picked hodrushite with about 15 % of hematite (sample 1) gave a density $6{\cdot}18 \pm 0{\cdot}03$ g/cm³. The recalculated density of pure hodrushite is then in the order of 6·35 g/cm³.

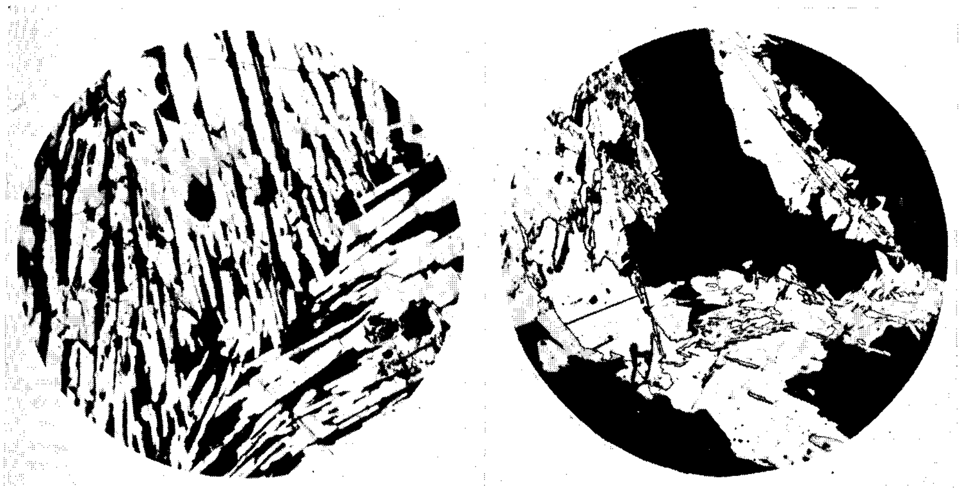
Microscopical characteristics. Hodrushite only rarely forms needle-shaped or lath-shaped idiomorphic grains in quartz (fig. 1). Regularly it occurs as irregular grains in hematite, representing relics of hodrushite after an intensive replacement by hematite. Locally (mainly in the fourth period) fine chalcopyrite lamellae occur in hodrushite grains (fig. 2).

In polished section hodrushite has a creamy colour with a very slight pinkish tint without any internal reflections. Its bireflectance is very weak and observable only in oil immersion. Anisotropy (in greyish colours) in air or in oil immersion is also very feeble and more pronounced only in fine aggregates.

Diagnostic etching tests (with reagents in standard concentrations): HNO_3—gradually turning brown; KCN and $HgCl_2$—brown, sometimes with an iridescent coating; HCl—a feeble brown tint or negative; $FeCl_3$ and KOH—negative.

The reflectivity measurements were made at the Bureau de Recherches géologiques et minières in Orléans-La Source, France by Dr. G. Halahyjová-Andrusovová, C.Sc.

under the supervision of Professor C. Lévy. The apparatus used was constructed to the designs of J. Prouvost (1960) and uses a stabilized light source, prism monochromator, photomultiplier (maximum sensitivity at 5250 Å), and an electronic amplifier. Measurements were conducted at eleven regularly spaced points of the visible-light spectrum between 4200 and 6200 Å. Standard deviations were estimated to be less than 1 % of the values obtained. A sphalerite sample from Santander, Spain, of which the reflectivity had been calculated by J. Orcel (1936) was used as a standard. Measurements were conducted on several grains in freshly polished sections without relief or defects. The reflectivity of hodrushite has a maximum at 5800–6000 Å, in good accordance with the creamy colour of the mineral in reflected light.



FIGS. 1 and 2: Fig. 1 (left). Lath-shaped aggregates of hodrushite (white) in quartz (black). Polished section, × 106, parallel nicols. Photographed by L. Osvald. Fig. 2 (right). Hodrushite (white) intensively replaced by hematite (greyish) in quartz (black). Polished section, × 106, nicols parallel. Photographed by L. Osvald.

λ, Å	4200	4400	4600	4800	5000	5200	5400	5600	5800	6000	6200
$R_{\max}$	27·0	29·5	30·2	31·8	32·4	32·7	32·9	32·8	33·4	36·0	34·1
$R_{\min}$	26·2	28·3	29·5	30·7	31·5	31·6	31·0	31·4	32·0	34·6	33·4

Crystallography. Lattice constants of hodrushite were measured on rotation and Weissenberg photographs taken with a crystal of average diameter about 0·03 mm. The unit cell is monoclinic with parameters:[1] a 27·205±0·050 Å, b 3·927±0·015 Å, c 17·575±0·050 Å, $\beta = 92^\circ\ 9' \pm 10'$.

According to the extinction ($k+l = 2n$) the space groups $A2$, Am, and $A2/m$ are possible. As the distribution of intensities among the reflections of various h and l is the same for all layers with $k \equiv 0 \bmod 2$ and $k \equiv 1 \bmod 2$ respectively, only the

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[1] The β value for hodrushite in the article by Kupčík and Makovický (1968) is a misprint.

special positions of atoms with $y = 0$ or $\frac{1}{2}$ are occupied and a mirror plane parallel to (010) is present. The centrosymmetricity test showed that the projection ($h0l$) is hypercentrosymmetric. Based on these results $A2/m$ is the most probable space group of this compound. This was confirmed by the results of crystal-structure analysis.

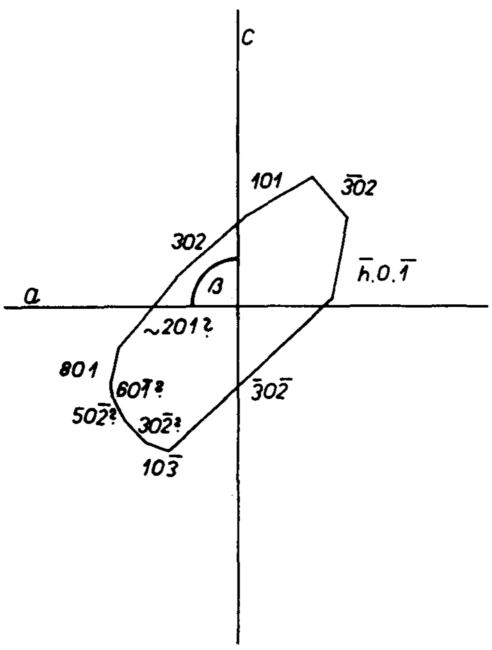

FIG. 3. An idealized cross-section of the hodrushite crystal perpendicular to the b axis.

Morphological measurements were difficult to make because of the very small crystal size, polysynthetic twinning, and imperfect development of crystal faces. The most perfect crystals used for determination of lattice constants were also used for morphological measurements. As their small size hindered the use of reflections from crystal faces measurements were made observing only the lustre of the faces, hence the accuracy of the data is rather low, about 1–2° for the best-developed faces.

The only faces developed on the crystals belong to the prismatic zone [010], the crystals being irregular at their ends; they have a columnar or acicular habit, being a little flattened in one direction. The best-developed faces belong to the form {302}. The mutual orientation of the lattice and morphology was determined on a Weissenberg goniometer.

Face	101	201(?)	302	$\bar{3}0\bar{2}$	$10\bar{3}$	$30\bar{2}$(?)	$\bar{3}02$	$60\bar{1}$(?)	$50\bar{2}$(?)	801	$h01$
ϕ_{obs}	191·13°	169·98	180·55	0·0	58·63	85·93	267·88	119·48	104·03	145·68	321·93
ϕ_{calc}	190·85	171·18	180·00	0·0	55·01	88·11	268·11	120·56	102·79	146·04	*

* 323·91° for $\overline{10}.0.\bar{1}$, 321·03° for $\overline{15}.0.\bar{1}$.

The X-ray powder pattern (table I) has the usual appearance for that of a sulphosalt mineral—a great number of mostly weak lines only a few of which are measurable. Indexing was made by computing the d-values of the strongest reflections on Weissenberg photographs. It showed that many of the lines are composed of several very closely spaced reflections so that the powder pattern can hardly be used for accurate lattice constant measurements in this case. The computed and measured d-values are in a very good accordance.

Chemical composition. An emission spectral analysis was made on a hodrushite concentrate that contained a considerable amount of inseparable hematite and minor quantities of other minerals intergrown with hodrushite. The main elements in the concentrate are Cu, Bi, Fe, Ca, Mg, and Al; those between 1 % and 0·01% are Pb, Ag, Si, and Zn; and trace elements are Au, Cd, Mn, W, Co, Hg, Mo, Sb, Sn, Ti, and V. It appeared possible that the Pb, Ag, and Sb might be substituted in the mineral, while the role of Fe was uncertain because of the hematite impurity.

TABLE I. *Powder diffraction data of hodrushite. 57 and 115 mm diam. powder cameras,* Cu-*K*α *radiation,* NaCl *internal standard; less intense reflections* (*as shown by single crystal data*) *given in parentheses*

d	*I*	*hkl*
4·38 Å	w/vw	$\bar{1}04$, 004
4·04	vw*	$\bar{3}04$, (602)
3·62	s	404
3·48	m	$\bar{5}04$, 702
3·22	m/s	$\bar{8}02$
3·102	vs	$\bar{3}13$, (511)
2·976	vw?	$\bar{7}04$, $\bar{4}13$, (900)
2·823	vw	$\bar{5}13$
2·715	s	711, ($\bar{4}06$)
2·545	m*	215, 506, $\bar{3}15$
2·450	vw?	$\bar{4}15$
2·382	vw?	$\bar{5}15$
2·301	vw	706, (813)
2·223	vw	615
2·160	w*	$\bar{3}08$, 12.0.2
2·104	w	117, $\bar{1}\bar{1}$.1.1, ($\bar{1}\bar{0}$.1.3, $\bar{1}17$)
2·048 Å	vw	317
2·003	w/vw	$\bar{9}$.1.15
1·947	w*	915, 517, 14.0.0
1·873	vw?	322, $\bar{8}08$
1·835	w	717
1·750	vw??	$\bar{1}19$, 019, 720
1·722	m	$\bar{3}19$, 219 424
1·688	vw??	4.0.10, ($\bar{1}\bar{0}$.1.7)
1·672	vw	$\bar{8}22$, (10.0.8)
1·643	?	$\bar{7}24$, 920
1·616	?	$\bar{7}$·0.10, $\bar{2}26$
1·607	vw	$\overline{16}$.0.4
1·575	vw?	824
1·566	vw??	?
1·539	vw?	(12.0.8)
1·487 Å	vw	726, (9.0.10)
1·450	w/m*	$\bar{3}28$, (12.2.2)
1·440	w	328, $\bar{4}$.0.12
1·419	vw	926, $\bar{6}$.1.11
1·402	w	14.1.7, 11.0.10
1·353	vw?	$\bar{8}28$, (11.2.6, $\bar{9}$.1.11)
1·323	vw	$\bar{1}\bar{5}$.2.2, $\overline{18}$.1.5, $\bar{1}\bar{4}$.1.9
1·273	vw	1.1.13, 10.2.8
1·250	vw	$\bar{2}\bar{0}$.0.6, $\bar{7}$.2.10
1·210	vw*	435, $\bar{2}\bar{1}$.1.3, $\bar{5}35$
1·159	m/w†	137, 14.1.11, 17.1.9, $\bar{1}\bar{0}$.3.3, $\bar{1}37$, ($\bar{4}$.2.12)
1·103	vw	$\bar{1}\bar{1}$.3.5
1·083	vw?	239, $\bar{3}39$, 139, $\bar{1}\bar{4}$.1.13

* broad. † doubled.

Two wet chemical analyses of hodrushite concentrate were made in the chemical laboratory of the Geological Research Institute, Comenius University, Bratislava, by Ing. V. Streško.

A final concentrate was prepared by dissolving quartz with hydrofluoric acid and then hand-separating hodrushite under a stereomicroscope. In spite of these precautions sample 1 contained a rather large amount of hematite and considerable admixture of intergrown chalcopyrite and wittichenite(?). Sample 2, checked under the microscope and by Weissenberg photographs of several crystals picked at random, contained hematite and some chalcopyrite lamellae as impurities.

Samples were dissolved in hot concentrated HCl (½ hour). Bismuth was separated from the other elements by strongly basic ion exchangers Anex L and Dowex 1. It was determined by a titration with EDTA solution. Copper was determined by two different methods: a titration with murexide and photometrically as the ammonia complex. In both these methods Bi was separated by ion exchange and Fe by ammonia. Iron was determined by permanganate and photometrically with ammonium thiocyanate; lead by a photometric method after an extraction with sodium diethyldithiocarbamate into chloroform and a re-extraction with copper sulphate. Silver was determined by atomic absorption, and sulphur in the first sample by precipitation of released H_2S in form of CdS and in the second sample in form of $BaSO_4$ after decomposition of the sample by heating with ZnO and Na_2CO_3.

Each of the determinations (except those of S in both samples) was conducted several times or by various methods. The result represents an average of the determinations.

The better of the two chemical analyses, no. 2, led to a formula $Cu_{7\cdot 50}Bi_{9\cdot 77}Pb_{0\cdot 16}Ag_{0\cdot 08}S_{22}$ with an unknown role of Fe in the chemical composition. Crystal-structure analysis led to a formula $Cu_8Bi_{10}Me_2S_{22}$ where *Me* represents metal atoms in a fairly regular octahedral position with atomic number equal to or slightly smaller than that of bismuth; it was assumed that it is principally Bi.

The large difference between the chemical and X-ray formulas of hodrushite led us to the use of electron-microprobe analysis for a determination of chemical composition of pure mineral. A detailed description of the analysis is published elsewhere (Makovický and McLean, in press), including a detailed discussion of correction procedures and results. Three different ways of theoretical corrections as well as the empirical Ziebold and Ogilvie (1964) correction formula were used. The results of theoretical corrections were further recorrected using Cu_2S, Bi_2S_3, and emplectite ($CuBiS_2$) as standards. The final formula accepted as the best estimate of chemical composition is

$$Cu_{8\cdot 12\pm 0\cdot 06}Bi_{11\cdot 54\pm 0\cdot 12}Fe_{0\cdot 29\pm 0\cdot 01}S_{22\cdot 00\pm 1\cdot 04},$$

which is in good agreement with the results of the crystal-structure analysis. Results for the other elements checked (Ag, Mn, Zn, Sb, Co, Ni) were found to be far below detectability limits. The maximum results for Pb, a less sensitive element, were 0·47 wt % Pb with standard deviation 0·25 wt %, which is just below the detectability

TABLE II. *Chemical analyses of hodrushite*

	1	2	3		1′	2′	3′		1″	2″	3″	
Bi	54·49	55·76	64·92	±0·55	63·84	62·53	66·09	±0·90	10·15	9·77	11·54	±0·12
Cu	12·83	13·01	13·88	0·08	15·03	14·59	14·13	0·17	7·88	7·50	8·12	0·06
Fe	—	—	0·44	0·01	—	—	0·45	0·01	—	†	0·29	0·01
S	18·04	19·23	18·98	0·89	21·13	21·56	19·33	0·93	[22]	[22]	[22]	
Fe_2O_3	15·09	6·28	—		—	—	—					
Sum	100·45	95·45*	93·23	±1·05	[100]	[100]*	[100]					

1. Sample 1, wet chemical analysis. Pb and Ag not determined.
2. Sample 2, wet chemical analysis; also Pb 0·93, Ag 0·24 %. Ca, Mg. Al, Si not determined. Ranges: Bi 55·56–56·22; Cu 12·84–13·23; Pb 0·92–0·95; Fe_2O_3 6·19–6·38 %.
3. Electron-probe microanalyses; Pb, Ag, Mn, Zn, Sb, Co, Ni all below detection limits.

1′, 2′, 3′. Analyses 1, 2, 3 recalculated to 100 %, after deduction of Fe_2O_3 in the case of anals. 1 and 2. 2′ includes Pb 1·04, Ag 0·27 %.

1″, 2″, 3″. Atomic ratios to 22 sulphur atoms; 2″ includes Pb 0·16, Ag. 0·08.

* Including Pb and Ag. † Also Pb and Ag.

limit for this element (approx. 0·5 wt % Pb); consequently Pb was not accepted into formula. The calculated density of hodrushite is 6·451 g/cm^3, in a good agreement with its measured density (6·35 g/cm^3).

Disagreement of the results of wet and electron-microprobe analysis is mainly due to inseparable micro-intergrowths of chalcopyrite, galena, etc., in the material analysed by the classical wet method.

Electron paramagnetic resonance of hodrushite was measured on an EPR spectrometer for a 3-cm wave zone with a sensitivity of 3×10^{11} spin/gauss with a high-frequency modulation of 500 kHz. The EPR measurement was carried out by Dr. Šurka in the Physics Department, Comenius University, Bratislava. No traces of resonance effect were found under conditions described above (whereas, for example, covelline gave a strong resonance effect), which can be explained either by absence of Cu^{2+} in sufficient concentration or by interaction of electron spins in the mineral, as in some other Cu sulphides (e.g. chalcopyrite).

Discussion. In many of its properties, particularly its powder pattern, hodrushite closely resembles cuprobismutite. However, while both minerals are monoclinic and have equal *b* axes and while *c* of hodrushite is very near to *a* of cuprobismutite, $a \sin \beta$ of hodrushite is 27·19 Å, whereas $2c \sin \beta$ of cuprobismutite is 29·96 Å, so that the cells are not commensurable. Through the kindness of Professor E. W. Nuffield of Toronto University we have been able to verify this conclusion also by comparing his Weissenberg photographs of cuprobismutite with our corresponding photographs of hodrushite: their geometry is quite distinct.

The resemblance between the powder photographs of cuprobismutite and hodrushite is explained on comparison of single-crystal photographs of the two minerals, which show that their distributions of X-ray intensities in reciprocal space are similar. This suggests that crystal structures of these minerals may have many common features. Kupčík and Makovický (1968) have determined the crystal structure of hodrushite, and found it to consist of two distinct layers packed alternately parallel to (100). One layer has the composition $Cu_8Bi_8Me_2S_{20}$, where *Me* is an octahedral position occupied mostly by Bi, and the dimensions of the cuprobismutite unit cell, while the other has distinct composition and dimensions. Hodrushite may therefore be regarded as a regular intergrowth of two layers, one of which resembles cuprobismutite. The relationship of the two minerals is rather similar to that found in the structures of sartorite, baumhauerite, and rathite (Nowacki and co-workers, 1961–5; Le Bihan, 1962; cf. also Makovický, 1967).

Single crystals of hodrushite show no evidence of a second phase or of order–disorder, and microprobe analyses at different points or areas of the hodrushite sample agree within the experimental error.

Hodrushite is thus a definite mineral species, though closely related to cuprobismutite and occuring in similar assemblages.

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