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ART. VIII.—*Gerhardtite and Artificial Basic Cupric Nitrates*, by H. L. WELLS and S. L. PENFIELD.*

WE shall describe in the present article a natural, crystallized basic cupric nitrate and a crystallized artificial salt of the same chemical composition but of different crystalline form. We also give an account of a re-investigation of two basic cupric nitrates to which have been ascribed different compositions, but which, as we shall show, have the same composition as the basic nitrates described by us and by other investigators, whose results will be briefly summarized.

GERHARDTITE, *a new mineral.*

This mineral was first identified as a new species by Prof. Geo. J. Brush, who found it among a lot of copper minerals from the United Verde Copper Mines, Jerome, Arizona, which were left at the Sheffield Scientific School by Mr. G. W. Stewart, assayer, from that place.

The single specimen in our possession consists of a small piece of very pure massive cuprite, along a crack in which the crystals of the nitrate occur, together with acicular crystals of malachite. The crystals, 4–6^{mm} in diameter, were few in number and were almost wholly sacrificed to obtain material for investigation. An attempt has been made to obtain more of the material, but as yet no other specimens have been received, although we are in hopes that more may be found at the locality. From the abundance of crystals on the specimen in our possession, it would seem that there must have been a quantity of it found. It was probably regarded as malachite by the miners. Another specimen contains crystals of atacamite on the cuprite.

The crystals, which were carefully separated from the cuprite, were subjected first to crystallographic, then to chemical examination. About 0·8 of a gram was obtained almost perfectly pure, the only impurity being a few acicular crystals of malachite which sometimes penetrated the nitrate but were visible only under the microscope.

The hardness of the mineral is 2. Specific gravity 3·426. Color dark green. Streak light green. Transparent.

The crystals after being detached were only fragmentary. All those suitable for measurement were reserved. They were very fragile and had to be separated and handled with very great care. The crystals are orthorhombic, having the habit shown

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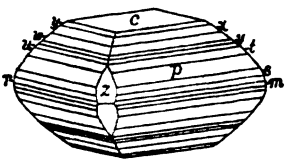
* The chemical work is by the former, the crystallographic by the latter.

in fig. 1. There are two cleavages, which serve for orientation, one basal, parallel to *c*, as perfect as the most perfect cleavage of gypsum, a second, less perfect, parallel to the macropinacoid. The crystals can be readily bent, in which case they crack and separate along the latter direction. The most prominent forms on the crystals, besides the basal plane, are a series of pyramids occurring in oscillatory combination, which makes their indentification somewhat difficult. The best measurements were obtained from a small but very perfect macrodome which was found on two crystals. Owing to the fragmentary nature of the crystals and the difficulty of identifying the pyramidal planes, their orthorhombic form might be doubted were it not for their optical properties.

1.



The axial ratio was obtained from the following measurements:

$$c \wedge z \quad 001 \wedge 201 = 68^\circ\ 16'$$
$$z \wedge p \quad 201 \wedge 111 = 39^\circ\ 3'\ 30''$$

giving $\breve{a} : b : \dot{c} = 0{\cdot}92175 : 1 : 1{\cdot}1562$

The following forms were observed:

c,	001,	*O*	*t*,	778,	$\frac{7}{8}$
z,	201,	$2\text{-}\bar{i}$	*u*,	334,	$\frac{3}{4}$
m,	110,	*I*	*v*,	7·7·10,	$\frac{7}{10}$
r,	551,	5	*w*,	223,	$\frac{2}{3}$
s,	221,	2	*x*,	13·13·20,	$\frac{13}{20}$
p,	111,	1	*y*,	112,	$\frac{1}{2}$

The following is the table of measured and calculated angles, the measurements being made on eight crystals, the number of times each form was measured being given.

		Calculated.	Measured.	No. of times.
$m \wedge m$	$110 \wedge 1\bar{1}0$	85° 20′		
$z \wedge z$	$201 \wedge 20\bar{1}$	43° 28′	43° 34′	1
$c \wedge m$	$001 \wedge 110$	90°	90° 15′–90° 25′	2
$c \wedge r$	$001 \wedge 551$	83° 19′	83° 1′	1
$c \wedge s$	$001 \wedge 221$	73° 40′	73° 53′	1
$c \wedge p$	$001 \wedge 111$	59° 37′	59° 23′–59° 57′	6
$c \wedge t$	$001 \wedge 778$	56° 11′	55° 57′–56° 19′	3
$c \wedge u$	$001 \wedge 334$	51° 59′	51° 52′–52° 20′	2
$c \wedge v$	$001 \wedge 7{\cdot}7{\cdot}10$	50° 3′	49° 46′–50° 38′	3
$c \wedge w$	$001 \wedge 223$	48° 40′	48° 8′–49° 12′	8
$c \wedge x$	$001 \wedge 13{\cdot}13{\cdot}20$	47° 57′	47° 11′–47° 56′	5
$c \wedge y$	$001 \wedge 112$	40° 28′	40° 13′–40° 18′	2
$x \wedge x$	$13{\cdot}13{\cdot}20 \wedge 13{\cdot}\bar{13}{\cdot}20$	60° 27′	60° 9′	1

Only distinct reflections were recorded, though other forms seemed to be present but were not definite enough to be determined. The variation in the measurements is large and may be due in part to an accidental bending of the crystals. The forms x and v with improbable indices would have been regarded as accidental had they not occurred repeatedly giving very distinct reflections. Tabular fragments, parallel to the basal cleavage, show under the polarizing microscope an extinction parallel to the macro-diagonal cleavage lines and in convergent light a bisectrix normal to c, 001. The optic axes lie in the brachypinacoid, the axial angle is large and could not be measured in air. Measured in the heavy solution of HgI_2 in KI ($n = 1{\cdot}703$ for yellow, $1{\cdot}722$ for green).

$$2H = 76° \ 20' \text{ for yellow.}$$
$$2H = 80° \ 4' \text{ for green.}$$
$$\text{Dispersion } \rho < v.$$

A very thin section had to be used to obtain the character of the dispersion as moderately thick sections were practically opaque to yellow light. The indices of refraction could not be determined owing to the want of suitable material, the Kohlrausch total-reflectometer giving no total reflection.

Double-refraction is strong, negative.

Pleochroism is distinct:

For vibrations parallel to 𝔠, $\breve{a}$ blue.
" " " " 𝔟, $\bar{b}$ green.
" " " " 𝔞, $\acute{c}$ green.

Chemical composition.—Qualitative examination showed only the presence of CuO, N_2O_5 and H_2O.

I. ·3975 gram yielded ·0457 H_2O and ·2634 CuO.
II. ·3986 gram yielded ·0449 H_2O, ·2646 CuO, and 19·7 cc. dry N at 12·8° and 759 mm. (cor.).

	Found. I.	Found. II.	Calculated for $4CuO . N_2O_5 . 3H_2O$.
H_2O	11·49	11·26	11·56
CuO	66·26	66·38	66·22
N_2O_5	22·25*	22·76	22·52
	100·00	100·40	100·00

Pyrognostics, &c. B.B. fuses at 2, coloring the flame green. With soda on coal easily reduced to metallic copper with deflagration. In closed tube gives nitrous fumes and water which reacts strongly acid. Soluble in dilute acids, insoluble in water.

It is somewhat surprising that a mineral of this composition has not been found before, owing to the occurrence of nitrates in natural waters, the stability and insolubility of the compound and the ease with which it is made artificially.

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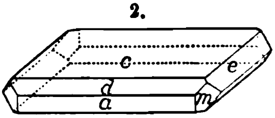
* By difference.

We propose for this beautiful and unique mineral, the only insoluble nitrate yet found in nature, the name Gerhardtite from the chemist who first determined the true composition of the same compound* made artificially.

Crystallized Artificial Basic Cupric Nitrate.

This is made by heating a solution of the normal nitrate with metallic copper in a sealed tube to about 150° for a day or more. The crystals form just above the surface of the liquid on the walls of the tube. When the contents of the tube are agitated the crystals fall to the bottom of the liquid where they remain undissolved while another crop is being formed. Cupric nitrite is apparently one of the products of the reaction; consequently the method is essentially a modification of that used by Vogel and Reischauer† in making the same compound in light, iridescent scales.

2.



The crystals are of a beautiful dark green color, exactly the same as that of the mineral, with a very brilliant luster. Specific gravity 3·378. The largest which we succeeded in making were 7 or 8^{mm} in length. Their form is monoclinic as is shown both by measurement and by their optical properties. Their habit is tabular, lengthened out in the direction of the b axis, fig. 2. The axial ratio was determined from the following measurements:

$$c \wedge a \quad 001 \wedge 100 = 85^\circ\ 27'$$
$$c \wedge d \quad 001 \wedge 101 = 48^\circ\ 25\tfrac{1}{2}'$$
$$e \wedge e \quad 011 \wedge 01\bar{1} = 82^\circ\ 41'$$

giving $\dot{a} : b : \dot{c} = \cdot 9190 : 1 : 1\cdot 1402$; $\beta = 85^\circ\ 27'$

The observed forms are

a,	100,	*i–ī*	*d*,	101,	1–ī
c,	001,	*O*	*e*,	011,	1–ì
m,	110,	*I*			

The following are the measured and calculated angles.

		Calculated.	Measured.
$m \wedge m$,	$110 \wedge 1\bar{1}0$	84° 59′	
$a \wedge m$,	$100 \wedge 110$	42° 29′	42° 36′
$c \wedge m$,	$001 \wedge 110$	86° 39′	86° 30′
	$00\bar{1} \wedge 110$	93° 21′	93° 40′
$c \wedge e$,	$001 \wedge 011$	48° 39′	48° 39′

Two twin crystals were found. They were not very perfect but the reëntrant angle $a \wedge a$ could be measured giving 9° 6′, calculated 9° 6′.

It may be said of the measurements on the prism m, that the face was usually quite imperfect and did not admit of very ac-

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* See beyond. † See beyond.

curate measurement. Many trials were made before crystals suitable for measurement were obtained and a few crystals only were selected, which although small were very perfect. Many of the crystals have a different habit from that given in fig. 2, being terminated at the extremity of the *b* axis by the prismatic faces only, but none were found which admitted of measurement.

The cleavage is basal, perfect, a second cleavage is parallel to *a* (100). The crystals are brittle but do not bend like those of the natural nitrate.

Under the polarizing microscope the crystals show an extinction parallel to the *b* axis. In convergent light the axes are seen to lie in the plane of symmetry. One axis is visible in the field of the microscope, inclined about 40° to a normal to the basal plane, the other axis is outside of the field of the instrument. The bisectrix lies in the obtuse secant; its inclination could not be determined. One of the largest tabular crystals showed one axis in the axial angle apparatus, the other was totally reflected. In the solution of HgI_2 in KI ($n=1{\cdot}703$ for yellow, $1{\cdot}722$ for green) both axes could be seen showing a marked inclined dispersion $\rho<v$, the axial angle being

$$2H = 59^\circ\ 22' \text{ for yellow.}$$
$$2H = 63^\circ\ 50' \text{ for green.}$$

Double-refraction, negative.

Pleochroism as in the orthorhombic crystals: || *b* green.
⊥ *b* blue.

The crystals of the natural and artificial compound are very much alike, making a very interesting case of dimorphism. The points of similarity are repeated below.

Orthorhombic, natural, $\breve{a}:\bar{b}:\dot{c} = 0{\cdot}92175:1:1{\cdot}1562$
$\beta = 90$
Cleavage 001 and 100

Monoclinic, artificial, $\grave{a}:b:\dot{c} = 0{\cdot}9190:1:1{\cdot}1402$
$\beta = 85^\circ\ 27'$
Cleavage 001 and 100.

Plane of the optic axes in the brachypinacoid in the former and in the corresponding plane of symmetry in the latter. Dispersion almost of the same amount and $\rho<v$ in both cases. Double-refraction negative, and pleochroism similar with almost identical shades of color in both.

Chemical analysis:

I. 1·2373 grams yielded ·1388 H_2O and ·8202 CuO.
II. ·5314 gram yielded ·0615 H_2O, ·3519 CuO, and 25·4 cc. dry N at 12·9° and 764 mm. (corrected).

	Found. I.	Found. II.	Calculated for $4CuO.N_2O_5.3H_2O$.
H_2O	11·23	11·57	11·26
CuO	66·29	66·22	66·22
N_2O_5	22·48*	22·10	22·52
	100·00	99·89	100·00

Artificial Basic Cupric Nitrate made by other methods.

Graham† investigated a compound made by heating normal cupric nitrate. His formula was incorrect, owing to the fact that he merely determined cupric oxide and volatile matter, and, consequently, had insufficient data for determining it.

Gerhardt‡ showed the true composition of Graham's compound to be $4CuO.N_2O_5.3H_2O$. He made it a number of times under varying conditions and always obtained analytical results corresponding to this formula. He also showed that the precipitate formed by adding ammonium hydroxide not in excess to a solution of the normal nitrate has the same composition.

The following investigators have since confirmed Gerhardt's results: Gladstone§ by analysis of the compound made by heating the normal nitrate; Kühn‖ by examination of the precipitate formed by ammonium hydroxide; Vogel and Reischauer¶ by investigation of the light, iridescent, blue-green, crystalline scales made by boiling mixtures of the solutions of cupric nitrate and potassium nitrite and also by boiling the deep green solution made by passing nitrous acid gas through water containing cupric hydroxide in suspension; Field,** and Reindel†† by examining the precipitate formed by the addition of potassium hydroxide, not in excess, to solutions of normal cupric nitrate.

On the other hand, Casselmann‡‡ has described a basic nitrate which is precipitated by boiling solutions of cupric nitrate with acetates and various other soluble salts of organic acids and to which he ascribes a composition corresponding to the formula $2(4CuO.N_2O_5)7H_2O$. It will be noticed that this differs from Gerhardt's formula by only $\frac{1}{2}H_2O$; hence we thought it proper to reinvestigate the compound.

Sodium acetate was added to a hot, dilute solution of cupric nitrate until a copious precipitate was formed. The liquid was boiled until the precipitate became dense when the latter was thoroughly washed with cold water. No discoloration of the product was noticed either on boiling or washing, although Cas-

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* By difference.

† Phil. Trans.. 1837, 57.

‡ Jour. Pr. Chem., xxxix, 136.

§ Idem, xliv, 184.

‖ Jahresber., 1, Engl. transl., p. 340.

¶ Jahresber., 1859, 216.

** Idem, 1862, 216.

†† Idem, 1867, 304.

‡‡ Zeitschr. Anal. Chem., 1865, 24.

selmann states that blackening took place in both instances when he made the compound, so that he was unable to make it pure and unaltered. The product was composed of minute crystals, forming a powder of a light green color. Specific gravity 3·371. The following chemical analysis proves its identity with the basic nitrate made by other methods.

Of the substance, dried over sulphuric acid, 1·0631 gram yielded ·1229 H_2O, ·7035 CuO, and 52·4 cc. dry N at 18·9° and 764 mm. (corrected).

	Found.	Calculated for $4CuO . N_2O_5 . 3H_2O$.	Calculated for Casselmann's formula.
H_2O	11·46	11·26	12·89
CuO	66·17	66·22	64·99
N_2O_5.......	22·42	22·52	22·12
	100·05	100·00	100·00

A basic cupric nitrate mixed with metalic silver was made by H. Rose* by acting on cuprous oxide with silver nitrate solution. Rose not having determined the composition of the salt, Rammelsberg† attempted to do so and assigned to it a composition represented by the formula $Cu_{10}N_6O_{25}$. This differs so widely from the basic salt made by all other known methods that it was deemed advisable to reëxamine it.

Pure cuprous oxide was made by adding a dilute solution of pure glucose to an excess of Fehling's solution heated just to boiling. The precipitate was thoroughly washed, then treated while still wet with a large excess of silver nitrate solution, the liquid was boiled and the whole allowed to digest on a water-bath for several hours. The resulting dark gray voluminous powder was carefully washed with water and dried at 100°. In some preliminary experiments it was found difficult to completely decompose cuprous oxide after it had been dried, and it was also found that the reaction took place only very slowly in the cold; consequently the above mentioned method for making the mixture was adopted.

Supposing the mixture to consist of a basic cupric nitrate of Gerhardt's composition and metallic silver, the reaction would evidently be as follows:

$$3Cu_2O+6AgNO_3+3H_2O=4CuO.N_2O_5.3H_2O+6Ag+2CuN_2O_6.$$

Analysis proved this to be the case.

Of the substance dried at 100°,

I. 1·4958 grams yielded by ignition 1·2848 Ag and CuO,—the latter yielded 1·1459 AgCl.

II. 1·9329 grams yielded 1·6592 Ag and CuO, 1·4791 AgCl, ·0893 H_2O, and 40·55 cc. dry N at 18·2° and 758 mm. (cor.)

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* Pogg. Ann., ci, 513.

† Ber. Deutsch. Chem. Ges., 1877, 1780.

	Found.			Calculated for $6Ag+4CuO.N_2O_5.3H_2O$.	
	I.	II.			
Ag	57·66	57·60		57·46	
CuO	28·23	28·24	66·68	28·17	66.22
H_2O		4·62	10·91	4·79	11·26
N_2O_5		9·49	22·41	9·58	22·52
		99·95	100·00	100·00	100·00

Graham* states that the basic cupric nitrate will withstand a temperature near that of melting lead without decomposition. We find, on the other hand, that it begins to decompose when heated to 180–200°, blackening and giving off both water and nitric acid. The product made in sealed tubes and that made by Casselmann's method were both subjected to this experiment with like results.

The empirical formula for the compounds under consideration is $H_6Cu_4N_2O_{12}$ or $H_3Cu_2NO_6$. Cooke† developes this to $(HO)_3$, $(CuO_2H)_3$, CuO_2, viii, N_2O. A simpler formula is $H(HOCu)_2NO_4$. The latter has the argument in its favor that some other basic nitrates can best be formulated as derivatives of the hypothetical acid H_3NO_4 (corresponding to H_3PO_4), but the union of hydroxyl to both acid and basic radicals is possibly an objection to it as well as to Cooke's symbol.

It is an interesting fact that the monoclinic (?) mineral tagilite has the formula $4CuO.P_2O_5.3H_2O$, exactly corresponding to the nitrate.

Method of analysis.

Owing to the small quantity (less than ·8 gram) of the native nitrate at our disposal, it was important to use a method which would give a complete analysis on a single sample. The apparatus having been set up and tested, it was found to be so satisfactory and convenient that it was used for the other analyses given in this article.

The substance was ignited in a boat in a current of pure, dry CO_2 in a combustion-tube. The CuO remaining in the boat was weighed. The gases passed over a hot roll of copper gauze, then through a weighed calcium chloride tube, which absorbed the water, into an azotometer containing a concentrated solution of potassium hydroxide where the nitrogen was measured.

The carbon dioxide was made from crystallized calcite. The removal of the air from the apparatus before the ignition and the collection of the nitrogen afterwards was accomplished by passing the CO_2 only about ½ hour in each case. The CO_2 in the $CaCl_2$ tube was replaced by dry air before weighing.

Laboratories of Chemistry and Mineralogy,
Sheffield Scientific School, June 6, 1885.

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* Loc. cit.

† Chemical Philosophy, 379.