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Claringbullite, a new hydrated copper chloride

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SUMMARY. Claringbullite, $Cu_4Cl(OH)_7.nH_2O$ where n is about 0·5, a new mineral, is reported as soft blue plates in cuprite from Nchanga open pit, Zambia and Kambowe, Mina M'sesa, Katanga. The mineral is hexagonal a 6·6708, c 9·183 Å, $Z = 2$. Optically, claringbullite is uniaxial negative with $\omega = 1{\cdot}782$ and $\varepsilon = 1{\cdot}780$. Indexed powder data are given together with five electron-probe analyses of the mineral.

IN 1973 a specimen of cuprite said to have come from the Nchanga open pit,[1] Zambia, with tiny blue platy crystals on one corner, was brought to the Museum for identification by Mr. N. Wilson. The blue crystals were thought to be gerhardtite, $Cu_2NO_3(OH)_3$, but their X-ray powder pattern did not correspond to this, or any other known mineral. A match was obtained, however, with a blue mineral from Bisbee, Arizona, belonging to Dr. S. A. Williams. A few days later a blue mineral from the M'sesa mine, Kambowe, Katanga, on loan from the Sorbonne, Paris, and believed to be a new species, was X-rayed and its powder pattern found to be identical with that of the Zambian and Arizonan mineral.

The Zambian and Katangan specimens form the type specimens of claringbullite, $Cu_4Cl(OH)_7.nH_2O$ where n is about 0·5. The mineral is named for Sir Frank Claringbull, former director of the British Museum (Natural History) and Keeper of Mineralogy. The data that follow and the name have been approved prior to publication by the Commission on New Minerals and Mineral Names, I.M.A.

Physical and optical properties. Claringbullite from Nchanga occurs as a slightly divergent group of blue plates filling a cavity in quartz and malachite on cuprite. Yellow-stained quartz crystals also occur on the specimen. The Katangan occurrence consists of slightly divergent groups of soft blue plates up to 1 mm across, with pearly lustre, in a vug in cuprite, associated with acicular and tabular crystals of brochantite. Malachite and copper occur elsewhere on the specimen. The claringbullite plates are flattened on {0001}; cleavage is perfect on {0001}; distinct on $\{10\bar{1}0\}$ and $\{11\bar{2}0\}$. Fragments from the Katangan specimen were used for the optical investigation and consist of micaceous, thin, delicate laminae with maximum dimensions from 0·05 to 0·28 mm. The mineral is uniaxial negative. In transmitted light it is pale blue with no noticeable pleochroism and ω_{Na} is 1·782 for sodium light. All cleavage flakes remained dark between crossed polars.

A cleavage flake of size 0·28 × 0·17 × 0·015 mm was mounted on a stage rotation apparatus. When viewed edgewise it remained pale blue for the principal vibration directions, but it was not possible to determine the refractive index for the extraordinary ray using the immersion method because of the micaceous nature of the fragment. Between crossed polars the edge-on flake showed straight extinction and abnormal interference colours of dark blue rising to yellowish-green. The yellowish-green interference colour was obtained when the 0·17 mm dimensions of the cleavage flake was parallel to the axis of the microscope and was judged to be first-order

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[1] S. Korowski, personal communication, believes that the specimen comes from the Nchanga deep mine, not the open pit.

yellow masked by the blue body-colour of the mineral. From the relative retardation of 275–400 mμ the birefringence was calculated as 0·002 ($\pm$0·0004). Claringbullite is thus uniaxial negative $\omega = 1{\cdot}782$, $\varepsilon = 1{\cdot}780$. Because of its low birefringence and the thinness of the plates, satisfactory interference figures could not be obtained.

By immersing a grain of Katangan claringbullite in dilute Clerici solution, its density was estimated to be close to 3·9 g.cm^{-3}.

Chemical investigation. Electron-probe analyses of five grains of claringbullite, obtained with a Cambridge Geoscan, are given, after correction, in Table I. Analyses 1–3 are of grains from the Zambian specimen, 4 and 5 from the Katangan specimen, and 6 represents ideal $Cu_4Cl(OH)_7.\frac{1}{2}H_2O$. The standards used were pure copper, sylvine (Cl), and anglesite (S). The Katangan and, to a lesser extent, the Zambian grains were unstable under the electron beam, so the analyses were obtained by using a defocused beam and moving the specimen after each count. The water figures were obtained by difference. However, in a direct determination, a small sample ($\sim$ 100 μg) of the Katangan material gave a bound-water figure of 14·3 % on a Perkin Elmer 240 elemental analyser. An infra-red absorption spectrum was obtained from a KBr disc. All the absorptions were very weak and those present were assigned to trace amounts of nitrate (1385, 1399 cm^{-1}) and sulphate (1070 cm^{-1}). Silicate, phosphate, arsenate, and carbonate anions were not detected. An absorption at 1653 cm^{-1} showed that some of the OH (3450 cm^{-1}) was present as H_2O. This water is thought to be zeolitic in nature, hence the introduction of *n* in the formula. Nitrogen was not detected when the water determination was made, establishing the N_2O_5 content as less than 1 %; it was not within the range of elements detectable in our electron probe. On the basis of eight copper atoms per formula unit, the formula derived from the mean of analyses 1–5 is $Cu_{8\cdot00}(SO_4)_{0\cdot01}Cl_{1\cdot99}(OH)_{14\cdot00}.0{\cdot}68H_2O$.

TABLE I. *Electron probe analyses of claringbullite*

	1	2	3	4	5	6
CuO	78·18	79·89	79·58	74·42	82·70	76·18
SO_3	0·06	0·08	0·08	0·12	0·12	—
Cl	8·55	8·71	8·84	8·30	8·20	8·49
H_2O*	[15·14]	[13·28]	[13·49]	[19·03]	[20·83]	17·26
Less O ≡ Cl	1·93	1·96	1·99	1·87	1·85	1·93
Sum	100·00	100·00	100·00	100·00	100·00	100·00

1, 2, and 3. Nchanga open pit, Zambia.
4 and 5. Kambowe, Mina M'sesa, Katanga.
6. Theory for $Cu_4Cl(OH)_7.\frac{1}{2}H_2O$.
* By difference.

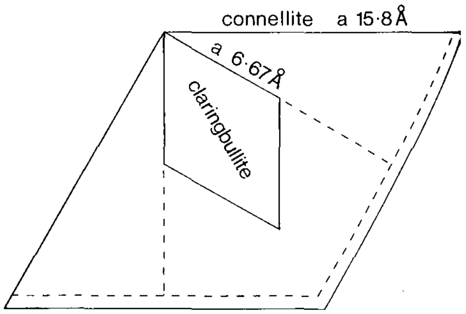

FIG. 1. Comparison of unit cells of connellite and claringbullite.

X-ray investigation. An apparently isotropic flake from the Zambian specimen was mounted vertically on a glass fibre; 15° oscillation and rotation photographs gave a layer line spacing of 6·65 Å and some evidence of hexagonal symmetry. Using a Bunn chart for hexagonal crystals it was possible to index the first two dozen lines of an 11·46 cm powder pattern for log $c/a = 0{\cdot}140$, $c/a = 1{\cdot}38$. Referring to Donnay and Ondik (1973) some similarity to the connellite–buttgenbachite group was shown, but the claringbullite powder patterns were different. A further photograph with a prolonged exposure time failed to reveal any intermediate layer lines. Zero and first-layer Weissenberg photographs around the same axis confirmed the hexagonal symmetry and gave a *c*-axis dimension of 9·16 Å, very close to those of connellite and buttgenbachite. The relationship between the cell dimensions of connellite-buttgenbachite and claringbullite is shown diagrammatically in fig. 1. The a dimensions are related by a factor $\sqrt{3}/4$:

Connellite-buttgenbachite $a = 15{\cdot}82$, $a\sqrt{3}/4 = 6{\cdot}85$ $c = 9{\cdot}14$ Å
Claringbullite $a = 6{\cdot}671$ $c = 9{\cdot}183$ Å

Systematic absences of $\{000l\}$ reflections with l odd were observed and there seems to be a tendency for $hh2hl$ reflections with l odd to be missing. Possible space groups are therefore $P6_3$, $P6_3/m$, $P6_322$, $P6_3mc$, $P\bar{6}2c$, or $P6_3/mmc$. Using the refinement method of Hess (1951) our trial indexing was confirmed and it was eventually possible to index all observed lines of the powder patterns. Final refinement of the cell dimensions of claringbullite for both specimens was obtained by a high-angle graphical extrapolation method, employing the Nelson-Riley function, and the results agree within the experimental error, giving a $6{\cdot}6708 \pm 0{\cdot}0003$, c $9{\cdot}183 \pm 0{\cdot}002$ Å. Indexed powder data are given in Table II. The density of the mineral, calculated from the mean analysis, is 3·99, and 3·92 g.cm^{-3} for ideal $Cu_4Cl(OH)_7.\frac{1}{2}H_2O$. As mentioned earlier the measured density is near 3·9 g.cm^{-3}. From the cell volume, chemical analysis, and density, it follows that the formula is $Cu_4Cl(OH)_7.nH_2O$ with $Z = 2$.

TABLE II. *X-ray powder data for claringbullite*

hkil	d_{calc}	d_{obs}	*I*	*hkil*	d_{calc}	d_{obs}	*I*	*hkil*	d_{calc}	d_{obs}	*I*
0001	9·18			$20\bar{2}5$	1·549	1·540	vvw	0008	1·148		
$10\bar{1}0$	5·77	5·75	vvs	0006	1·530			$32\bar{5}4$	1·147	1·148	vw
$10\bar{1}1$	4·89	4·89	s	$31\bar{4}2$	1·512	1·514	w	$50\bar{5}1$	1·146		
0002	4·59	4·58	s	$10\bar{1}6$	1·479	1·475	vvwb	$40\bar{4}5$	1·135		
$10\bar{1}2$	3·59	3·59	mw	$30\bar{3}4$	1·475			$22\bar{4}6$	1·127	1·126	vvw
$11\bar{2}0$	3·334	3·336	w	$22\bar{4}3$	1·464			$10\bar{1}8$	1·125		
$11\bar{2}1$	3·134			$40\bar{4}0$	1·444	1·445	w	$21\bar{3}7$	1·124		
$20\bar{2}0$	2·887	2·889	ms	$40\bar{4}1$	1·426			$50\bar{5}2$	1·120		
$20\bar{2}1$	2·754			$31\bar{4}3$	1·419			$33\bar{6}0$	1·111		
$10\bar{1}3$	2·704	2·700	vvs	$21\bar{3}5$	1·405			$42\bar{6}0$	1·091	1·092	w
$11\bar{2}2$	2·698			$11\bar{2}6$	1·391	1·392	w	$50\bar{5}3$	1·080	1·080	vvw
$20\bar{2}2$	2·444	2·445	vs	$40\bar{4}2$	1·377	1·378	mw	$33\bar{6}2$	1·080		
0004	2·295	2·276	m	$20\bar{2}6$	1·352	1·352	ms	$20\bar{2}8$	1·066	1·066	vvw
$11\bar{2}3$	2·254			$22\bar{4}4$	1·349			$42\bar{6}2$	1·062	1·062	mw
$21\bar{3}0$	2·183	2·178	vvw	$30\bar{3}5$	1·329	1·327	vw	$40\bar{4}6$	1·050	1·050	w
$10\bar{1}4$	2·133	2·133	mw	$32\bar{5}0$	1·325			$41\bar{5}5$	1·039	1·038	vvw
$21\bar{3}1$	2·123			$31\bar{4}4$	1·313	1·313	vvw	$51\bar{6}0$	1·037		
$20\bar{2}3$	2·100	2·099	w	$32\bar{5}1$	1·311			$50\bar{5}4$	1·032		
$21\bar{3}2$	1·971			$40\bar{4}3$	1·306			$22\bar{4}7$	1·031	1·032	vw
$30\bar{3}0$	1·925			$10\bar{1}7$	1·279	1·274	vvwb	$51\bar{6}1$	1·030		
$11\bar{2}4$	1·890	1·891	vw	$32\bar{5}2$	1·273			$21\bar{3}8$	1·016	1·016	vvw
$30\bar{3}1$	1·884			$41\bar{5}0$	1·260			$31\bar{4}7$	1·015		
$20\bar{2}4$	1·797	1·797	ms	$21\bar{3}6$	1·253	1·253	vvw	$30\bar{3}8$	0·9864	0·9863	mw
$21\bar{3}3$	1·777	1·775	m	$41\bar{5}1$	1·248			$42\bar{6}4$	0·9863		
$30\bar{3}2$	1·775			$22\bar{4}5$	1·234			$41\bar{5}6$	0·9734	0·9732	vvw
$10\bar{1}5$	1·750	1·749	vvw	$40\bar{4}4$	1·222	1·223	w	$60\bar{6}0$	0·9631	0·9632	vvw
$22\bar{4}0$	1·667	1·669	ms	$11\bar{2}7$	1·220			$20\bar{2}9$	0·9625		
$22\bar{4}1$	1·640			$32\bar{5}3$	1·216	1·216	mw	$22\bar{4}8$	0·9459	0·9459	w
$30\bar{3}3$	1·629	1·630	vw	$41\bar{5}2$	1·215			$51\bar{6}4$	0·9458		
$11\bar{2}5$	1·608	1·604	vw	$31\bar{4}5$	1·207			$31\bar{4}8$	0·9335	0·9332	vw
$31\bar{4}0$	1·602			$30\bar{3}6$	1·198	1·198	vvw	$50\bar{5}6$	0·9225	0·9225	vvw
$21\bar{3}4$	1·582	1·583	mw	$21\bar{2}7$	1·194			$43\bar{7}3$	0·9074		
$31\bar{4}1$	1·578			$41\bar{5}3$	1·165			$10\bar{1}10$	0·9073	0·9071	vw
$22\bar{4}2$	1·567	1·568	w	$50\bar{5}0$	1·155			$52\bar{7}2$	0·9071		
								$33\bar{6}6$	0·8998	0·8998	vw
								$40\bar{4}8$	0·8990	0·8988	vvw

Type specimens. The specimen of claringbullite from Zambia is registered in the British Museum (Natural History) collection as BM 1976, 109. The Katangan specimen is the property of the Sorbonne, Paris.

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