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Structures of Some Tetragonal Sheet Silicates.*

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The phases $CaCuSi_4O_{10}$ ('Egyptian blue'), $SrCuSi_4O_{10}$ and $BaCuSi_4O_{10}$ have been grown in single crystals. Their structure, in the space group *P4/ncc*, is similar to that of gillespite, $BaFeSi_4O_{10}$, previously established (Pabst, 1943). The parameters of the structure have been determined for $CaCuSi_4O_{10}$ by means of repeated electron-density projections onto (100) and (110) followed by further adjustments.

Gillespite is not known in good crystals. Each of the three artificial materials was obtained in measurable crystals showing the forms {001}, {101}, and {110} in the order of prominence predicted by the rule of Donnay & Harker (1937).

Gillespite is easily attacked by mineral acids. The copper analogues are impervious to attack. This may be attributed to the superior stability of copper in 4-fold planar coordination. Such coordination is characteristic of divalent copper but exceptional for ferrous iron.

It seems probable that the imperfectly described mineral cuprorivaite is the natural analogue of 'Egyptian blue'.

Introduction

'Egyptian blue' is a material known from ancient times. According to Micault (1881) it was mentioned by Pliny and its manufacture was described by Vitruvius. In the 1880's samples of the material found in France were examined by several mineralogists. Fouqué (1889) established the composition as $CaCuSi_4O_{10}$ and synthesized single crystals, the ancient materials having been no more than frits. He reported the crystal system, density, optic sign and pleochroism. Laurie, McLintock & Miles (1914) again synthesized the material and reported refractive indices. Jope & Huse (1940) reported the identification of 'Egyptian blue' from various sources by means of powder diffraction patterns but gave no numerical data of any sort. Crystals of Egyptian blue, formed in the refractory bricks of a copper smelting furnace were described by Ivanov, Zvetkov & Shumilo (1938) and Belov (1942) reported that it had a structure with Si_2O_5 sheets 'like those in apophyllite' but gave no details or numerical data.

Synthesis

Sintering of pellets prepared in a press from finely ground mixtures of $CaCO_3$, CuO and amorphous silica in the proportions 1:1:4 yielded a microcrystalline aggregate which furnished powder patterns showing that the expected phase had formed. In attempts to produce single crystals small amounts of various fluxes were added to the starting materials. A pellet containing about 10% of borax upon heating to about 800 °C. for a day and slow cooling was found to be changed to a blue crystalline aggregate with a small amount of interstitial glass and a remnant of flux. After leaching with HCl and gentle crushing perfect platy tetragonal crystals, about 0·1 × 0·03 mm. could be selected. Crystals of the corresponding strontium and barium compounds were made in the same manner.

Physical constants

Crystals of all three materials were studied by reflection goniometry, under immersion in polarized light and by means of calibrated Weissenberg patterns (Pabst, 1957) and precession patterns. This was accomplished without dismounting the crystals by means of adapters for the X-ray goniometer heads and small immersion cells for the polarizing microscope simplified from the design described by Fisher (1952). Densities of the new phases were determined by suspension of crystals in suitably diluted Clerici solutions and determination of the density of the liquids by Westphal balance. Table 1 lists cell dimensions, density and optical properties for the three newly synthesized phases and related materials, the data being taken in part from earlier publications.

Cell dimensions increase regularly from the CaCu to the BaCu phase, those of the latter differing but slightly from the cell dimensions of gillespite. It is noteworthy that the refractive indices of the Sr and Ba compounds are below those of Egyptian blue. This is in accord with the known 'specific refractive energies' for the constituents. The birefringence of the cupric silicates is about 20 times that of gillespite and is surely attributable to the difference in the influence of Cu^{+2} and of Fe^{+2} on this property. The pleochroism shows the expected correspondence.

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Table 1. *Data for 'Egyptian blue' and related materials*

	Egyptian blue $CaCuSi_4O_{10}$	$SrCuSi_4O_{10}$	$BaCuSi_4O_{10}$	Gillespite $BaFeSi_4O_{10}$	Leached Gillespite $8\,SiO_2 . 5\,H_2O$ (S.2)
a_0 (Å)	7·30 ± 0·01*	7·37 ± 0·01	7·44 ± 0·01	7·51 ± 0·01 (P.1)	7·64 ± 0·03 (P.2)
c_0 (Å)	15·12 ± 0·02	15·57 ± 0·02	16·11 ± 0·02	16·07 ± 0·02	15·10 ± 0·05
Density g.cm.$^{-3}$ obs.	3·06 ± 0·03 3·04 (F.)	3·32 ± 0·03	3·47 ± 0·03	3·402 ± 0·004	2·05 (P.2)
Density g.cm.$^{-3}$ calc.†	3·09	3·32	3·52	3·407	2·15
N_o	1·636 ± 0·003 '1·635(4)' (L.)	1·628	1·632	1·621 (S.1)	1·449 (S.2)
N_e	1·591 '1·605(3)' (L.)	1·588	1·593	1·619 (S.1)	1·441 (S.2)
$N_o - N_e$	0·045 '0·031' (F.)	0·040	0·039	0·002	0·008
$(2N_o + N_e)/3$	1·621	1·615	1·620	1·620	
N_{mean} (calc.)‡	1·627	1·625	1·628	1·636	
Pleochroism					
O	'bleu intense' (F.)	blue	blue	'rose red' (S.1)	colorless
E	'rose pale'	pale—colorless	pale—colorless	'pale pink'	

	Cuprorivaite (M.)
Density	2·866
N_o	1·627
N_e	1·590
O	blue
E	pale yellow

Data taken from literature

(F.)	Fouqué, 1889
(L.)	Laurie, McLintock & Miles, 1914
(S.1)	Schaller, 1922
(S.2)	Schaller, 1929
(M.)	Minguzzi, 1938
(P.1)	Pabst, 1943
(P.2)	Pabst, 1958

* The wave-length of Cu $K\alpha_1$ radiation having been taken to be 1·54051 Å.

† For ideal cell contents of 4 formula weights for gillespite, Egyptian blue and its analogues and 2 formula weights for leached gillespite.

‡ Calculated from the rule of Gladstone and Dale, using 'specific refractive energies' tabulated by Larsen & Berman (1934, p. 31).

Structure determination

From the published descriptions it seemed likely that Egyptian blue would be found to have a structure similar to that established for the mineral gillespite, $BaFeSi_4O_{10}$, by Pabst (1943). Single crystal diffraction patterns of the three new copper silicates show that they all crystallize in the space group $P4/ncc\text{–}D_{4h}^{8}$ and that they are isostructural with gillespite. As might be expected, the closest correspondence is seen between patterns of gillespite ($BaFeSi_4O_{10}$) and $BaCuSi_4O_{10}$. The Sr and Ca compounds show some departures in the intensities. Trial calculations showed that these depend not only on the substitution of lighter ions for Ba^{+2} but also involve some changes in the atomic parameters. Some systematic intensity changes may be seen in the powder patterns of the three materials recorded in Table 2, in which indexed lines are listed in order of decreasing spacings for $CaCuSi_4O_{10}$. This is not the order of decreasing spacing for $SrCuSi_4O_{10}$ lines following 2·331 Å or $BaCuSi_4O_{10}$ lines following 2·733 Å underlined in Table 2. The intensities recorded in the table were determined by comparison with a scale of standard intensities with films made from powder mounts free from orientation effects. Patterns made from ordinary powder mounts with preferred orientation of particles show markedly different intensity relations.

The structure of gillespite had been determined very largely by 'trial and error' methods, supplemented by an electron-density projection onto (001) and a one-dimensional summation from F_{00l}'s (Pabst, 1943, Figs. 3 and 4). In gillespite Ba^{+2} has 24·7% of the scattering power for X-rays at 0° θ, whereas in Egyptian blue Ca^{+2} in a position corresponding to that of Ba^{+2} in gillespite has 9·7% of the scattering power at 0°. Clearly Egyptian blue is more favorable for the accurate determination of the twelve parameters of the structure.

Intensity data were collected for Egyptian blue by means of $0kl$, hhl and $hk0$ Weissenberg and precession patterns made with Cu and with Mo radiation. Patterns made with both filtered and unfiltered radiation were used for the intensity estimates based on comparison with a scale of graded exposures made by multiple oscillation of a crystal. Observations were made on several crystals and exposures were extended to as much as 40 hr. A check on the relative intensities of the stronger low angle reflections was obtained by photometry of powder patterns. Care was taken to use preparations in which preferred orientation of the platy materials was at a minimum.

After some trials it was found that comparing observed F's obtained partly with Cu and partly with Mo radiation with calculated F's is unsatisfactory in this case because of the large $\Delta f'$, 2·1, of Cu with

Table 2. *Powder diffraction patterns of 'Egyptian blue' and related materials*

	$CaCuSi_4O_{10}$			$SrCuSi_4O_{10}$			$BaCuSi_4O_{10}$		
hkl	I_0	d_o (Å)	d_c (Å)	I_0	d_o (Å)	d_c (Å)	I_0	d_o (Å)	d_c (Å)
002	4	7·63	7·56	5	7·82	7·79	6	8·06	8·06
102	1½	5·22	5·25	½	5·36	5·35	½	5·42	5·47
110			5·16			5·21	1½	5·25	5·26
112			4·26	4	4·33	4·33	7	4·42	4·40
004	9	3·78	3·78	3	3·88	3·89	1	4·03	4·03
200	2½	3·66	3·65	< ½	3·68	3·68	½	3·72	3·72
104	8	3·36	3·36	5	3·44	3·44	2½	3·55	3·54
202	10	3·29	3·29	10	3·34	3·33	10	3·38	3·38
211	5	3·19	3·19	3	3·23	3·22			3·26
114	4	3·05	3·05	6	3·12	3·12	8	3·20	3·20
212	9	3·00	3·00	7	3·04	3·04	4	3·08	3·08
213	½	2·736	2·740			2·782			2·828
204	4	2·629	2·626	4	2·675	2·676	4	2·733	2·733
220	4	2·585	2·581	5	2·607	2·606	5	2·629	2·630
006	½	2·518	2·520			2·595	1	2·690	2·685
214	½	2·471	2·471			2·515			2·565
222			2·442	2	2·478	2·471	2	2·497	2·500
106	2	2·386	2·382	½	2·452	2·448			2·526
302	3	2·321	2·316			2·343	1	2·361	{ 2·370
310			2·308			2·331			2·353
311			2·282			2·305			2·328
116	5	2·270	2·265	4	2·322	2·323	4	2·391	2·392
215			2·218			2·263			2·315
312			2·208	3	2·231	2·233	3	2·261	2·258
224	1	2·136	2·132	2	2·167	2·165	1	2·206	2·202
313			2·099			2·126			2·155
206	½	2·069	2·074			2·122			2·177
304			2·051			2·078			2·112
321	2	2·007	2·007	< ½	2·036	2·027			2·047
216			1·995	1	2·041	2·039	½	2·091	2·089
314	2	1·970	1·970	3	2·000	1·999	3	2·030	2·032
322			1·956			1·977			2·005
008	1½	1·890	1·890	1	1·949	1·946	½	2·019	2·014
323			1·879			1·902			1·926
315			1·835			1·866			1·900
108	6	1·831	1·830	1	1·882	1·882	1½	1·947	1·944
	4	1·784		3	1·845		1	1·885	
	2	1·758		1	1·830		2	1·862	
	4	1·704		½	1·814		½	1·840	
	2	1·636		½	1·781		3½	1·770	
	4*B*	1·603		3	1·737		½	1·663	
	½*d*	1·573		2	1·650		2½	1·630	
	1	1·528		< ½	1·627		1½	1·606	
	1	1·483		3	1·612		1½	1·523	
	½	1·462		2	1·585		2	1·481	
	½	1·456		½	1·524		1	1·440	
	½	1·435		1	1·496		2	1·371	
	½	1·426		½	1·469		½	1·343	
	2	1·398		2	1·437		½	1·318	
	2	1·380		1	1·408		< ½	1·294	
	2½	1·336		½	1·393		1½	1·282	
	1	1·315		1½	1·352		1½	1·196	

plus 15 or more additional lines in each pattern, mostly weak and diffuse.

Cu $K\alpha$ rays (Templeton, 1955; Dauben & Templeton, 1955). Accordingly observed F's used in the final calculations, as given in Table 4, were the averages taken from the best Mo precession patterns available for each of the zones considered with the exception of F_o002 which was obtainable only from Cu patterns. Absorption corrections were not applied since the crystals used were exceedingly small. L. & P. corrections were applied by the use of a Waser chart for zero layer precession patterns supplemented by calculations for a few spots near the limits of the patterns for which corrections cannot be read closely from the chart.

Though the electron-density projection onto (001) is not favorable for the determination of atomic coordinates, inspection of the known structure of gillespite showed that good resolution of the peaks was to be expected in projections onto (100) and (110). Signs of observed F's were chosen for $0kl$ and hhl reflections in accord with those of calculated F's for $CaCuSi_4O_{10}$

Table 3. *Observed and calculated structure factors*

$0k\ l$	F_o	F_c
	(R 11·3) (R' 14·9)	
00 0	—	740
00 2	63	+74
01 2	38	−29
00 4	201	−219
01 4	161	−145
02 2	175	+162
02 4	88	+95
00 6	51	−41
01 6	74	−69
03 2	83	−87
02 6	55	−47
03 4	—	−2
00 8	114	+124
01 8	104	+117
04 2	55	+56
03 6	19	+26
02 8	57	−47
04 4	58	−45
0010	52	−64
03 8	—	−22
0110	92	+105
04 6	—	−4
05 2	—	+5
0210	146	+159
05 4	60	−67
04 8	64	+57
0310	49	+40
05 6	35	−34
0012	114	+127
0112	—	−24
06 2	57	+47
0212	54	+45
0410	—	+14
06 4	45	+39
05 8	70	+71
0312	58	+52
06 6	—	−4
0014	142	+152
0114	60	−55
0510	45	+46
0412	78	+70
0214	—	+1
07 2	40	−44
06 8	—	−1
07 4	37	−41
0314	53	−54
07 6	—	+2
0512	29	−26
0610	41	+39
0016	—	−14
0116	29	−32
0414	81	+70
0216	41	+41
07 8	26	+36
08 2	58	+62
08 4	—	−25
0316	67	−61
0612	60	+63
0514	—	−20
0710	33	+26
08 6	—	−18
0018	94	−90
0416	—	+18
0118	—	−12
08 8	—	−6
0218	25	+32
0614	22	+32
09 2	60	−70
0712	—	0
0318	36	+30
0516	—	−11
09 4	33	−35
0810	42	+41
09 6	—	+16
0418	23	−28
0020	—	+38
0120	—	+25
0714	—	−16
0616	—	+4
09 8	—	+23
0220	51	−40
0812	66	+61
0102	49	+35
0104	53	+58
0910	32	+36

$hk0$	F_o	F_c
	(R 15·0) (R' 20·0)	
110	37	−41
200	71	−61
220	152	+165
310	32	+14
400	232	+213
330	15	−25
420	113	+135
510	19	−32
440	54	+31
530	18	−34
600	39	+46
620	65	+51
550	—	−1
710	—	−9
640	134	+132
730	—	−17
800	84	+96
820	85	+85
660	—	+8
750	—	−26
840	—	+37
910	—	−34
930	—	−13
770	—	+4
860	112	+106
1000	—	+11
1020	48	+41
950	—	−6

$hh\ l$	F_o	F_c
	(R 11·5) (R' 13·5)	
11 2	—	+8
11 4	112	+113
22 2	40	+43
11 6	118	+133
22 4	56	+46
22 6	10	+8
11 8	96	+86
33 2	—	−9
33 4	92	+96
22 8	—	+4
1110	—	+11
33 6	90	+85
2210	20	−7
44 2	48	+53
33 8	76	+78
1112	16	−21
44 4	33	+47
44 6	14	−23
2212	135	+125
3310	—	+6
44 8	24	+19
1114	—	−4
55 2	—	−2
3312	—	−17
2214	85	+76
55 4	62	+63
4410	51	+65
55 6	51	+39
1116	40	+44
3314	—	−15
55 8	50	+51
4412	35	+31
2216	18	−26
66 2	71	+67
5510	—	+6
66 4	47	+54
1118	60	+61
3316	49	+51
4414	—	+9
66 6	74	−67
2218	31	−28
5512	—	+7
66 8	28	−20
4416	35	+43
3318	52	+54
1120	44	+43
6610	92	+90
5514	—	−6
77 2	—	−3
2220	60	+50
77 4	32	+40

using the parameters determined for gillespite (Pabst, 1943). Fourier summations were carried out on these two series after modifying indices by substituting $l/2$ for l since the space group, $P4/ncc$, restricts these series to reflections for which l is even. This is comparable to the procedure used previously (Pabst, 1943, p. 384) for the one-dimensional summation on gillespite. It allows the determination of electron densities at 120th's of c_0 with the use of strips or cards in terms of 60ths. For the $0kl$ summation systematic sign changes were first made to correspond to shift of the origin from the $\bar{4}$ position, used in describing the gillespite structure and retained for the description of Egyptian blue, in order to gain the convenience of a center of symmetry at the origin of the (100) projection. No preliminary shift of origin is required for this purpose for the hhl summation as projection yields a center of symmetry at the origin of (110). In each case summation had to be carried out over only one eighth of the projection. Due to the appearance of two equivalent peaks for atoms in general positions in each of these projections all parameters can be read from either one of them if overlap does not interfere. Coordinates were obtained from the (110) projections in a manner similar to that used by MacGillavry, Hoogschagen & Sixma (1948, p. 874) and by Romers, Ketelaar & MacGillavry (1951, p. 115).

Summations were carried out by means of punched cards and IBM equipment. The first pair of projections indicated modifications of 11 of the 12 parameters, involving sign changes for $5F_{hhl}$'s and $7F_{0kl}$'s. A second pair of projections using the changed signs indicated further changes not exceeding 0·005 in 6 of the parameters. Renewed calculation of F's caused 2 more sign changes among F_{hhl}'s and 3 among F_{0kl}'s, one of these a reversal of a previous change. All 5 of these changes applied only to unobserved F's so that no improvement could be achieved by pursuing the course followed thus far. During this process the R values had dropped from 46·2 to 24·9% for hhl's and from 45·7 to 23·0% for $0kl$'s, unobserved reflections being counted as having half the threshold intensity.

Separate 'temperature factors' were now calculated for the $0kl$, hhl, $00l$ and $hk0$ series. $0k0$ and $hh0$ which had been included in the series previously used were now transferred to the $hk0$ group not hitherto considered. Inspection of the remaining discrepancies between calculated and observed F_{00l}'s indicated the possibility of further small adjustments in z values. The value of 'B' in the temperature factor found for $0kl$'s and hhl's was nearly the same, close to 0·6 Å^2. The indicated value for $hk0$'s was 0·4. These values are not far from that recently found for the related substance $BaSi_2O_5$, sanbornite, by Douglass (1958, p. 522). The slightly lower value of B for the $hk0$ series might be expected for a material with a pronounced sheet structure but the paucity of data leaves the significance of the difference in doubt and so B was taken as 0·6 for all series in the final calculations.

Calculated and observed F's together with R values of the several series of reflections are given in Table 3. The F_o values in each series have been adjusted to a common sum with the corresponding F_c values after application of the temperature correction. f-values for Ca^{+2}, Si^{+4} and O^{-2} were taken from *ITDCS*; for Cu^{+2} the values for Cu were modified for ionization in the range of $\sin\theta/\lambda$ 0·0 to 0·2. The overall value of R, omitting unobserved reflections, is 12·0%. R', counting unobserved reflections at half the corresponding F_c, is 15·5 for all reflections. The R' value for $hk0$'s in Table 3 is still rather high. This is due to the fact that a group of $hk0$'s for which the calculated value of F is of such order that they might be observed if the L. & P. factor were favorable fall into the region of the Mo precession pattern in which this factor is most unfavorable.

The quality of the intensity estimation was tested by comparing several sets of values of F_o obtained from different patterns or groups of patterns. A set of F_o's for hhl obtained as an average from 4 films showed differences from the set of F_o's from a single one of the films after adjustment to a common summation corresponding to an R value of 11·5, while a similar comparison of F's obtained from two $hk0$ patterns led to an R of 10·3 after exclusion of three reflections not observed on both films. Clearly any attempt to improve the agreement shown in Table 3 would be meaningful only if based on better estimates of intensities.

Table 4. *Atomic parameters in Egyptian blue,* $CaCuSi_4O_{10}$, *P4/ncc*

Atoms	Position	x	y	z	Symmetry
4 Ca	*b*	0	0	0	$\bar{4}$
4 Cu	*c*	0	½	0·082	4
16 Si	*g*	0·255	0·170	0·148	1
8 O_I	*f*	0·205	0·205	¼	2
16 O_{II}	*g*	0·455	0·245	0·128	1
16 O_{III}	*g*	0·115	0·265	0·082	1

The final set of atomic parameters is shown in Table 4. x and y values are given to 1/200th of a_0 and z values to 1/500th of c_0, corresponding to 0·036 and 0·030 Å respectively.

Structure, chemical and physical properties

The structure of Egyptian blue shows no marked difference from that of gillespite which has been pictured in *Structure Reports* Vol. 9, p. 250, 1955, and in a paper by Pabst (1958, Figs. 4 and 4, pp. 975 and 978) dealing with the structure of leached gillespite. Within the height of one cell there are two Si_8O_{20} sheets of linked, Si-centered, tetrahedra parallel to (001). Each tetrahedron has one unshared corner, there being 4 such on each side of each sheet with the area a_0^2. The Cu atoms are at the centers of squares formed by the oxygens at 4 such unshared corners. The Ba atoms are situated in 8-fold coordination midway between sheets.

Table 5. *Interionic distances in Egyptian blue,* $CaCuSi_4O_{10}$, *P4/ncc*

Si–O_I	1·60 Å	Shortest O–O distance between oxygens of different tetrahedra within same sheet	
Si–O_{III}	1·60		
Si–$O_{II'}$	1·59		
Si–O_{III}	1·59	O_{II}–O_{II}	4·27 Å
Edges of SiO_4 tetrahedra		Shortest O–O distances between sheets	
O_I–O_{III}	2·66	O_{III}–O_{II}	3·22 Å
O_I–O_{II}	2·62	O_{III}–O_{III}	3·27
O_I–$O_{II'}$	2·61	Cu–O_{III}	4 at 1·91
O_{II}–O_{II}	2·57	Ca–O_{III}	4 at 2·45
O_{III}–O_{II}	2·58	Ca–O_{II}	4 at 2·70
O_{III}–$O_{II'}$	2·58	Next shortest Ca–O distance	
		Ca–O_{III}	4 at 3·52 Å

Note:—To identify distances within one tetrahedron it is necessary to distinguish the two symmetrically equivalent O_{II} in it. Referring to the lower tetrahedron shown in Fig. 1, $O_{II'}$ is the oxygen whose coordinates are $x = 0{\cdot}455$, $y = 0{\cdot}245$, the origin being taken in the upper left corner.

Interionic distances are shown in Table 5. They are close to expected values but are all subject to an uncertainty of about ± 0·03 to 0·04 Å. The differences in parameters from those of gillespite, like the differences in cell dimensions, are probably due mostly to the difference in radius between Ba^{+2} and Ca^{+2}. The several distances listed in Table 4 may be identified in Fig. 1 which shows a small segment of the structure.

In spite of the close similarity of their structures gillespite and Egyptian blue show contrasting chemical behavior. Gillespite may be readily leached by cold dilute HCl with the total removal of Ba and Fe (Schaller, 1929). The residue of hydrated silica has been shown to retain the principal features of the Si_8O_{20} sheets of gillespite (Pabst, 1958). Egyptian blue or its Sr and Ba analogues can be subjected to the action of HCl for months without showing the slightest

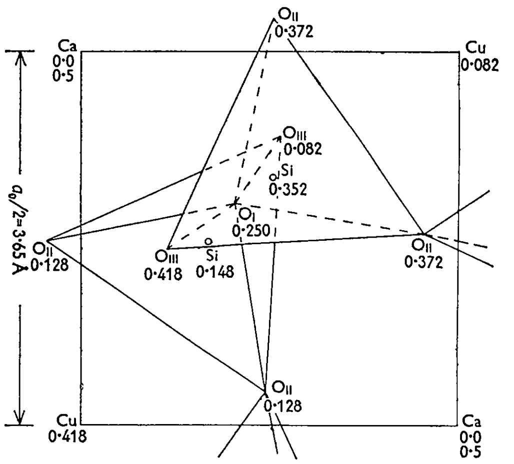

Fig. 1. Orthographic projection of one eighth of the unit cell of $CaCuSi_4O_{10}$ onto (001). *z* coordinates are given for all atoms. Oxygen tetrahedra about Si are outlined. Only the corners at O_{III}'s are not shared.

sign of chemical attack. The difference is surely due to the substitution of Cu for Fe in square planar coordination. That this is the preferred coordination for Cu^{+2} was first emphasized by Harker (1936) in a paper partly entitled 'Square quadricovalent cupric copper'. The tendency of cupric ions to form such a coordination is so strong that even in structures related to the *C*6 (cadmium iodide) type they are situated at the centers of squares of anions at a minimum distance (Helmholz, 1947). Examples of structures with Cu^{+2} in square planar coordination have recently been reviewed by Wells (1949), and by Nowacki & Scheiddeger (1952).

In the structures reviewed by these authors Cu^{+2} is invariably surrounded by four anions at a minimum distance at the corners of a square, or nearly so. In addition two more anions at much greater distances lying on or near the normal to the plane of the square are considered as belonging to the Cu coordination and this is sometimes called a distorted octahedral coordination. In the case of Egyptian blue there are no anions of any sort on the normals to the squares of oxygens about Cu and this might be considered as the ideal case of 'square quadricovalent cupric copper'.

In gillespite Fe^{+2} is in this same simple square coordination. But Fe^{+2} is rarely found in other than regular octahedral coordination. At best it might be considered as having an incomplete or degenerate octahedral coordination in gillespite, abnormal for iron. This is doubtless the reason gillespite is so readily leached by acid while Egyptian blue resists attack.

Structures have been described with various other cations, for instance Pt, Pd and Ni (Brasseur & de Rassenfosse, 1938), forming four coplanar bonds. This suggests that still other analogues of gillespite might be made in the same fashion as the cupric phases. Attempts to produce CaNi or BaNi disilicate by sintering were unsuccessful. There is some indication from the work of Curtiss, Lyle & Lingafelter (1952) that Ni may not form the square planar coordination in cases where this is found in the corresponding cupric compound. Further efforts are planned to determine what substitutions are possible in the gillespite type of structure.

The connection of the perfect {001} cleavage of gillespite with the sheet structure is obvious. Schaller (1929) also reported another 'much poorer' cleavage which he designated (100) and 'a suggestion of a very poor third cleavage after *m*(110)'. Since Schaller observed no pyramidal forms he had no sure means of distinguishing first and second order prismatic cleavage. Either of these would involve rupture of bonds in the Si_8O_{20} sheets. The linkage in these sheets is such that the {110} cleavage would require breaking of 2 bonds between tetrahedra per $\sqrt{(2)}a_0.c_0/2$ Å², whereas {100} cleavage would require breaking two such bonds per $a_0.c_0/2$ Å². The former is favored by these relations. In the few cases where distinct prismatic cleavage was seen in gillespite and its direction established by X-rays it was found to be {110} cleavage.

Morphology

Egyptian blue and its Sr and Ba analogues were all obtained as good crystals. They invariably showed the combination of forms pictured in the idealized drawing of a $BaCuSi_4O_{10}$ crystal in Fig. 2. It may be seen that the morphology is precisely that predicted from the rule of Donnay & Harker (1937).

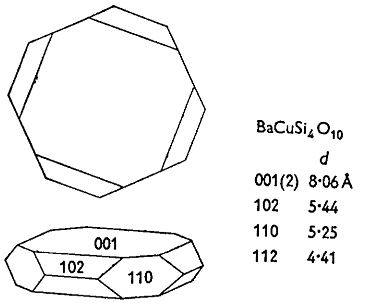

Fig. 2. Idealized drawing of a typical crystal of $BaCuSi_4O_{10}$ showing correspondence of habit to that predicted according to Donnay & Harker (1937).

Ivanov, Zvetkov & Shumilo (1938) reported for Egyptian blue that 'the crystals show a tendency to produce lamellar forms along the basopinacoid' and listed the forms {110}, {100}, {111}, {101} and {001} referred to the axial ratio $c/a=0{\cdot}74447$. This value multiplied by $2\sqrt{2}$ is 2·106, close to $c_0/a_0=2{\cdot}071$ of this study. The suggested transformation from Ivanov *et al.* to Pabst is $\frac{1}{2}\frac{1}{2}0/\bar{\frac{1}{2}}\frac{1}{2}0/002$. The transformed indices of the forms reported by Ivanov *et al.* become: {100}, {110}, {102}, {114} and {001}. The additional forms, {100} and {114}, reported by these authors are the 5th and 9th respectively in a Donnay–Harker list.

Possible natural counterpart

As shown in Table 1 the properties of the very rare mineral, cuprorivaite, described by Minguzzi (1938) as a slightly hydrous calcium copper disilicate with some minor substituents, are so close to those of Egyptian blue that it seems probable that the two are analogues. Some commentators have not recognized cuprorivaite as a valid mineral species. Unfortunately authenticated specimens have not been available for a check.

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Die Kristallstruktur von α-Cu(NH$_3$)$_2$Br$_2$

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The two forms of Cu(NH$_3$)$_2$Br$_2$ exist. The α-form is monoclinic with

$$a = 8{\cdot}18,\quad b = 8{\cdot}15,\quad c = 4{\cdot}05\ \text{Å};\quad \beta = 94{\cdot}8°;$$

space group $C2/m$; $Z = 2$. The structure of the cubic β-form has been previously described.

The structure of α-Cu(NH$_3$)$_2$Br$_2$ has been determined from powder pattern with the aid of special methods. Planar centrosymmetrical molecules of Cu(NH$_3$)$_2$Br$_2$ are present, with Cu–Br: 2·54 Å, Cu–N: 1·93 Å, ∢ Br–Cu–N: 90°. A close relation to the structure of β-Cu(NH$_3$)$_2$Br$_2$ is also explained.

Einleitung

Die Existenz zweier Formen des Diammin-Kupferdibromids Cu(NH$_3$)$_2$Br$_2$ wurde vor kurzem von Gažo (1959) nachgewiesen. Diese zwei Formen, α- und β-Cu(NH$_3$)$_2$Br$_2$, unterscheiden sich durch ihre Farbe, ihre Zersetzungstemperatur, sowie durch verschiedene Löslichkeit in organischen Lösungsmitteln. Beide geben verschiedene Pulverdiagramme. α-Cu(NH$_3$)$_2$Br$_2$ entsteht in Form eines lichtgrünen Pulvers, wenn man einen Strom von trockenem NH$_3$ in eine Lösung von Cu(NO$_3$)$_2$ und LiBr in Aceton einleitet. β-Cu(NH$_3$)$_2$Br$_2$ erhält man in Form eines olivgrünen Pulvers aus Cu(NH$_3$)$_6$Br$_2$ bei vorsichtigem Erwärmen.

Löst man α- oder β-Cu(NH$_3$)$_2$Br$_2$-Pulver in einer konzentrierten wässrigen Lösung von NH$_4$Br und lässt diese Lösung langsam verdunsten, so entstehen immer olivgrüne nadelförmige Kristalle Cu(NH$_3$)$_2$Br$_2$ kubi-