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The crystal structure of chlorotionite, $CuK_2Cl_2SO_4$ *

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Auszug

Chlorothionit, $CuK_2Cl_2SO_4$ hat die Raumgruppe *Pnma*; die Gitterkonstanten sind $a = 7{,}732(15)$, $b = 6{,}078(1)$, $c = 16{,}292(3)$ Å; $Z = 4$. Die Struktur wurde mit direkten Methoden bestimmt. Atomparameter und anisotrope Temperaturfaktoren wurden nach der Methode der kleinsten Quadrate bis zu $R = 0{,}032$ für 893 beobachtete Reflexe verfeinert.

Die Koordination der Cu-Atome ist pseudooktaedrisch. Diese Pseudooktaeder vereinigen sich zu Doppelketten der Zusammensetzung $^{\infty}_{1}[Cu_2Cl_4O_4]^{8-}$. Jedes SO_4-Tetraeder beteiligt sich mit einer Kante an einem Cu-Pseudooktaeder. In der asymmetrischen Einheit befinden sich zwei verschiedene K-Atome. Die $^{\infty}_{1}[Cu_2Cl_4O_4]^{8-}$-Doppelketten sind durch diese miteinander verbunden.

Abstract

Chlorotionite, $CuK_2Cl_2SO_4$, is orthorhombic, space group *Pnma* with $Z = 4$. The unit-cell dimensions are: $a = 7.732 \pm 0.0015$, $b = 6.078 \pm 0.001$, $c = 16.292 \pm 0.003$. The crystal structure has been determined by direct methods and refined by least-squares to an R value of 0.032 for 893 measured reflections.

Cu atom is surrounded by four chlorine and two oxygen atoms to form a pseudo-octahedron in $[4 + 2]$ coordination. Cl(1)—Cl(1) edges are shared by $[CuCl_4O_2]$ pseudo-octahedra which build a double chain running along b axis, whose repeat unit is $^{\infty}_{1}[Cu_2Cl_4O_4]^{8-}$. Cu pseudo-octahedra and SO_4 tetrahedra are linked via two oxygen atoms to form a more complex structural unit of composition $^{\infty}_{1}[Cu_2Cl_4O_4(SO_4)_2]^{12-}$. The two symmetrically independent K atoms are six-coordinated by four oxygen and two chlorine atoms and provide the connection among the copper and sulphate polyhedra chains.

Introduction

Chlorotionite is an halogen sulphate of potassium and copper, first described by Scacchi (1872). Owing to symmetry and colour similarity this mineral is sometimes mistaken for euchlorine. Natural

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crystals of chlorotionite were chemically studied by SCACCHI (1872) and by ZAMBONINI (1935) and artificial ones by BELLANCA (1946). The chemical analyses are not in complete agreement, essentially with respect to the Cu and K content. For the artificial chlorotionite BELLANCA deduced the following formula: $K_2SO_4CuCl_2$. Data on x-ray crystallography were provided also by BELLANCA, who assigned to chlorotionite the space group *Pnma* and cell parameters $a = 6.105$, $b = 16.132$, $c = 7.697$ Å with $Z = 4$.

Experimental

The best crystals among those available for structural study were found in a sample coming from Vesuvius, eruption 1906 (Mineralogical Museum, University of Bari). They occur in crystalline aggregate associated with other unidentified minerals. As no x-ray powder pattern is quoted in the mineralogical files of JCPDS, chlorotionite crystals were identified comparing our lattice parameters with those given by BELLANCA. Lattice constants were determined from Weissenberg photographs and refined by application of the least-squares method using data from x-ray powder pattern. The values so

Table 1. *X-ray powder pattern of chlorotionite*

Philips powder diffractometer, Ni-filtered Cu Kα radiation, NaF as internal standard

$h\,k\,l$	$d_{\rm cal}$	$d_{\rm obs}$	I
1 0 1	6.980	6.98	9
0 1 1	5.698	5.69	29
1 1 1	4.589	4.58	12
0 0 4	4.073	4.073	8
0 1 3	4.049	4.049	12
2 0 1	3.760	3.761	14
2 1 0	3.263	3.262	29
2 0 3	3.149	3.149	21
0 2 0	3.039	3.039	100
0 2 2	2.846	2.847	33
1 2 2	2.671	2.672	14
2 0 5	2.491	2.491	21
2 2 3	2.187	2.187	71
2 0 7	1.994	1.994	19
2 2 5	1.927	1.927	14
3 1 5	1.918	1.918	12

determined are: $a = 7.732 \pm 0.0015$, $b = 6.078 \pm 0.001$, $c = 16.292 \pm 0.003$ Å. The indexed powder pattern is given in Table 1. Indexing was done taking into account the intensities of Weissenberg pictures. Our experimental density, obtained by the method of the heavy liquids, is 2.69 g cm^{-3}, which well agrees with 2.67 and 2.673 g cm^{-3} given by SCACCHI and BELLANCA. The sample used for the intensity data collection had a prismatic orthorhombic habit elongated in the [010] direction. The intensities were measured by Philips PW 1100 computer-controlled four-circles diffractometer, using Mo$K\alpha$ radiation and graphite monochromator. The ω-2θ scan technique was used. The rate of scanning was 0.05° s^{-1}, and the scan range was 2°. The intensities were measured up to $2\theta = 60°$. A total of 1212 independent reflections were measured. Of these 319 weak reflections with $(I_{\text{top}} - 2\sqrt{I_{\text{top}}}) < I_{\text{back}}$ were omitted (I_{top} is the intensity in counts s^{-1} measured at the maximum of reflection during the first scan, I_{back} is the mean of two preliminary background measurements of 5 sec). To unobserved reflections a conventional value equivalent to

Table 2. *Fractional atomic coordinates with standard deviations in parentheses*

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Cu	0.6212(1)	$\frac{3}{4}$	0.4615(1)	S	0.6296(2)	$\frac{3}{4}$	0.3024(1)
K(1)	0.3821(2)	$\frac{1}{4}$	0.2808(1)	O(1)	0.7758(7)	$\frac{3}{4}$	0.3629(4)
K(2)	0.1193(2)	$\frac{3}{4}$	0.4050(1)	O(2)	0.6324(7)	0.9481(6)	0.2518(3)
Cl(1)	0.6026(2)	$\frac{1}{4}$	0.5485(1)	O(3)	0.4752(7)	$\frac{3}{4}$	0.3587(4)
Cl(2)	0.8402(2)	$\frac{3}{4}$	0.5526(1)				

Table 3. *Final anisotropic temperature factors for all atoms in chlorotionite*
Standard deviations are in parentheses

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	β_H*
Cu	0.0039(1)	0.0175(3)	0.0011(0)	0	0	0	1.55
K(1)	52(2)	111(4)	36(1)	0	4(1)	0	2.26
K(2)	57(2)	110(4)	15(1)	0	− 1(1)	0	1.51
Cl(1)	57(3)	157(6)	13(1)	0	− 4(1)	0	1.70
Cl(2)	63(3)	114(5)	14(1)	0	− 7(1)	0	1.56
S	36(2)	81(4)	11(1)	0	− 2(1)	0	1.07
O(1)	28(8)	0.023 (2)	14(2)	0	1(3)	0	1.89
O(2)	87(7)	0.0060(8)	17(1)	− 0.0001(10)	− 6(2)	− 0.0007(3)	1.58
O(3)	31(8)	0.021 (2)	12(2)	0	5(3)	0	1.70

* β_H are the equivalent isotropic thermal parameters according to HAMILTON.

Table 4. *Observed and calculated structure factors. Values shown are multiplied by a factor of 10*

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
0	0	4	1039	1054	6	0	2	72	-75	2	1	18	474	-479	9	1	12	214	219	5	2	13	482	-475	3	3	3	92	-84
		6	944	-947			3	855	839	3	1	1	69	-44	10	1	0	648	646			14	155	167			4	353	349
		8	592	-626			5	619	602			2	45	37			2	68	79			16	119	-132			5	847	-849
		10	878	-877			7	516	516			3	173	147			3	146	153			18	65	91			6	766	762
		12	1057	-1060			9	325	321			4	492	-480			4	280	279			19	124	112			7	272	283
		14	551	-561			10	69	-59			5	1123	1126			6	173	-174	6	2	0	127	139			8	515	532
		16	288	-257			11	185	191			6	1030	-1022			8	273	-281			1	317	-311			9	45	-43
		18	162	-164			12	72	68			7	382	-381	0	2	2	1217	-1201			3	1017	-1002			11	259	264
		20	652	626			13	98	89			8	640	-660			4	105	-120			4	73	72			12	114	117
		22	367	358			15	368	-364			11	328	-332			6	137	147			5	300	-299			13	277	280
1	0	2	162	-144			16	158	164			12	124	-137			8	1079	1080			6	61	-69			14	444	-456
		3	29	-29			17	123	-132			13	349	-351			10	331	331			7	681	-676			16	130	-122
		4	39	32			19	636	-644			14	493	513			12	1251	1257			8	88	85			17	133	123
		5	1252	1309	7	0	1	131	139			15	58	-68			14	249	254			9	70	-82			18	82	-99
		6	526	-528			2	306	311			16	174	176			16	442	421			11	334	-339			19	60	78
		7	278	-304			3	200	-206			17	159	-149			20	471	-460			14	70	-76			20	66	-43
		8	952	-997			4	504	499			18	96	112			22	436	-424			15	227	217	4	3	0	233	-235
		9	282	-283			5	450	455			19	73	-95	1	2	1	736	-703			16	124	-125			1	168	-164
		10	350	-343			6	608	610			20	90	69			2	130	86			17	209	215			2	54	-58
		11	892	-917			8	812	828			21	166	-144			3	57	-29	7	2	1	113	-112			3	563	538
		12	176	-195			9	92	93	4	1	0	236	240			4	29	28			2	270	-275			4	64	-59
		13	508	-512			10	136	140			1	76	-73			5	1037	-1068			3	183	186			5	53	-33
		14	392	410			11	183	-199			2	135	134			6	432	431			4	435	-444			6	143	140
		17	184	-177			12	130	-125			3	406	-388			7	217	242			5	389	-407			7	362	347
		18	117	132			13	183	-176			5	321	-297			8	862	886			6	565	-556			9	392	-372
		20	305	295			14	520	-527			6	118	-122			9	276	268			8	737	-749			10	53	69
		21	63	83			15	63	59			7	228	-215			10	246	253			9	76	-70			11	543	542
		22	99	116			16	194	-183			8	66	-70			11	746	771			10	117	-124			13	419	408
2	0	1	1227	-1198			17	186	-186			9	241	225			12	206	219			11	150	153			15	64	62
		3	1659	-1657	8	0	0	1178	1185			11	492	-487			13	484	483			12	129	118			19	367	-352
		5	1989	-2001			1	110	-110			12	54	-62			14	394	-403			13	182	182	5	3	1	458	467
		6	58	54			3	205	205			13	630	-630			16	57	47			14	474	486			2	211	-210
		7	1018	-1010			4	330	337			15	61	55			17	182	180			15	84	-82			3	129	127
		9	378	-372			6	192	-172			19	498	490			18	126	-140			16	174	168			4	134	-115
		10	33	36			7	36	47			21	88	77			20	262	-244	8	2	0	922	-933			5	521	531
		11	124	-128			8	171	-171	5	1	1	588	-594			21	49	-57			2	154	-157			6	117	117
		13	153	-144			12	362	-362			2	262	256			22	117	-124			3	129	-132			7	326	-335
		15	833	816			13	82	87			3	178	-174	2	2	0	65	-62			4	174	-163			8	428	436
		16	110	-116			14	279	-285			4	135	109			1	218	227			8	274	280			9	287	-288
		17	361	362	9	0	1	433	445			5	644	-661			2	62	58			9	100	-102			10	117	112
		19	798	799			3	279	279			6	167	-159			3	2079	2058			10	139	-121			11	413	-422
3	0	1	40	0			4	125	120			7	407	410			4	49	-46			12	428	426			12	234	241
		2	122	117			5	456	458			8	550	-554			5	1122	1057			13	112	-115			13	325	-332
		3	187	-158			6	209	-206			9	337	341			7	1398	1375			14	162	173			14	131	-134
		4	689	-686			7	341	-347			10	151	-150			8	50	-57	9	2	1	389	-404			15	92	82
		5	1102	-1115			8	74	-84			11	522	528			9	115	-95			3	251	-247			16	95	109
		6	1155	-1139			9	304	-309			12	275	-289			11	441	440			4	113	-111			17	59	-22
		7	393	392			11	512	-515			13	378	384			13	117	-133			5	415	-428	6	3	0	974	955
		8	962	-982			12	165	-182			14	154	156			15	551	-539			6	177	178			3	170	176
		9	53	-60	10	0	0	136	147			15	68	-62			16	80	92			7	314	325			5	107	119
		10	112	-98			1	96	-103			16	105	-118			17	474	-483			8	79	87			8	175	-177
		11	282	285			2	91	102			19	89	- 85			19	625	-608			9	272	277			10	334	320
		12	133	-149			3	191	-187			20	172	162	3	2	1	30	19			11	468	481			11	82	-82
		13	441	427			5	246	-263	6	1	0	1400	-1384			2	96	-82	10	2	0	164	-174			12	355	-347
		14	543	550			6	58	-50			1	72	66			3	160	137			3	253	253			16	345	-341
		15	122	138			7	206	-195			2	171	150			4	586	579			4	54	-57	7	3	2	257	-261
		16	294	286			8	27	-20			3	253	-263			5	921	927			5	139	156			3	177	-180
		17	178	176	0	1	1	779	770			4	187	-176			6	977	960			6	77	83			4	123	-132
		18	181	195			3	702	634			5	82	-91			7	294	-297			7	238	250			5	486	498
		19	88	114			5	672	-668			6	103	93			8	869	874	0	3	1	51	-53			6	390	-386
		20	179	159			7	73	-76			8	73	63			10	70	72			3	923	-894			8	360	-384
		21	60	61			9	206	199			10	236	-214			11	207	-214			5	758	734			9	164	158
4	0	0	2507	-2643			11	576	590			11	50	56			12	145	144			7	297	-279			10	97	-75
		1	164	155			13	637	623			12	327	321			13	405	-415			9	171	158			11	210	-222
		2	363	-361			15	144	155			14	136	146			14	503	-518			11	674	-686			13	84	-99
		3	178	-176			17	206	203			16	333	328			15	67	-81			13	383	-368			14	345	366
		4	1229	-1180			19	719	-706			18	317	320			16	250	-240			15	256	-267	8	3	0	162	169
		5	79	74			21	215	-196	7	1	2	324	327			17	197	-191			17	93	-84			1	130	-126
		6	797	757	1	1	1	863	819			3	196	195			18	173	-183			19	520	511			3	461	-458
		8	743	727			2	122	102			4	159	169			19	73	-81			21	227	222			5	73	-71
		9	54	-51			3	47	-71			5	571	-581			20	144	-133	1	3	1	579	-561			6	99	-105
		10	235	237			4	40	34			6	465	464			21	88	-82			2	68	-61			7	282	-284
		11	84	-85			5	1036	1073			7	72	-81	4	2	0	1825	1821			4	50	-61			11	241	-241
		12	693	665			6	476	467			8	443	459			1	47	-50			5	764	-779			13	77	-63
		13	93	-99			7	332	-357			9	172	-168			2	791	765			6	378	-371	9	3	1	214	-215
		14	650	658			8	965	993			10	109	112			3	64	68			7	268	281			2	202	204
		16	308	298			9	265	-261			11	254	270			4	606	581			8	732	-745			3	78	-79
		18	53	52			10	182	183			13	128	131			6	300	-277			9	221	216			4	114	103
		20	467	-451			11	748	-779			14	397	-410			7	75	-70			10	112	-119			5	268	-288
		21	88	92			12	81	101			17	235	234			8	987	-968			11	570	590			7	201	211
5	0	1	787	-794			13	434	-439	8	1	0	141	-153			9	87	97			12	89	-97			8	213	-228
		2	57	-72			14	398	-415			1	245	254			10	82	67			13	369	367			9	137	130
		3	383	-371			15	128	119			2	70	-69			12	840	-822			14	355	361	10	3	0	518	-507
		4	198	-188			17	97	-82			3	452	451			13	134	128			15	138	-131			2	105	-103
		5	826	-823			18	66	-74			5	202	200			14	392	-409			16	66	-70			3	113	-109
		6	330	324			20	199	-186			6	87	81			16	418	-415			17	63	71			4	179	-183
		7	482	487	2	1	0	1672	1638			7	265	259			19	57	-65			20	146	143	0	4	2	444	443
		8	390	407			1	17	-26			11	209	211			20	336	322	2	3	0	902	-860			4	392	398
		9	448	436			2	793	-766			13	144	135	5	2	1	705	694			2	131	132			6	342	-349
		10	153	149			3	190	190			15	126	-125			2	73	73			3	105	-105			8	594	-596
		11	837	838			4	655	596	9	1	1	255	261			3	332	320			4	96	-95			10	331	-342
		12	257	266			5	70	68			2	234	-232			4	178	165			5	84	-83			12	776	-781
		13	528	522			6	324	-279			3	90	104			5	727	736			6	96	-98			14	273	-282
		14	137	-148			7	60	63			4	113	-101			6	266	-259			8	236	226			16	236	-225
		16	101	105			8	34	30			5	322	336			7	437	-440			10	866	-848			18	53	-56
		18	68	-76			10	778	764			7	242	-250			8	382	-385			11	78	77			20	450	426
		19	135	-118			11	70	-73			8	268	276			9	391	-392			12	323	324	1	4	1	425	426
		20	198	-196			12	220	-214			9	153	-150			10	109	-101			14	147	151			2	53	-43
6	0	0	72	-78			14	368	-375			10	55	62			11	761	-754			16	603	588			5	731	734
		1	673	650			16	391	-581			11	199	-215			12	269	-276			18	320	322			6	316	-323

Table 4. *(Continued)*

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
1	4	7	193	-204	5	4	8	247	252	1	5	5	510	525	5	5	6	66	-60	1	6	14	183	-204	0	7	13	193	-196
		8	547	-562			9	280	280			6	258	256			7	255	263	2	6	1	309	309	1	7	1	154	-167
		9	152	-149			10	85	84			7	222	-231			8	287	-292			3	643	623			5	307	-322
		10	171	-181			11	566	574			8	430	449			9	174	180			5	547	541			6	137	-137
		11	524	-553			12	191	201			9	126	-119			11	306	314			7	440	431			7	133	147
		12	149	-156			13	352	349			10	62	67			12	169	-173			11	96	99			8	249	-268
		13	334	-335			14	113	-117			11	384	-404			13	214	217			15	354	-346			9	71	82
		14	273	287			16	89	102			12	65	58			14	110	106	3	6	2	51	-15			11	203	223
		17	127	-118	6	4	1	352	344			13	229	-231			15	67	-63			4	158	175	2	7	0	351	-340
		20	203	199			3	635	620			14	247	-260	6	5	0	845	-825			5	421	430			2	183	167
2	4	1	455	-436			5	310	313			15	108	103			2	233	218			6	373	376			3	61	-53
		3	1129	-1083			6	36	29	2	5	0	905	879			3	169	-180			7	105	-123			8	71	73
		5	948	-904			7	399	402			2	487	-471			4	166	-157			8	377	387			10	434	-443
		7	784	-756			9	104	103			3	105	103			6	144	131			11	104	-88			12	104	108
		11	184	-188			11	188	189			4	353	345			10	157	-152			13	176	-180	3	7	4	88	90
		15	506	500			15	229	-222			6	211	-211			12	128	126			14	270	-285			5	336	-354
		17	282	282	7	4	2	184	193			8	105	108	7	5	2	171	180	4	6	0	1013	988			6	277	285
3	4	4	344	-349			3	155	-167			10	439	427			3	145	149			1	65	-62			7	109	111
		5	661	-668			4	320	323			14	226	-229			4	70	70			2	126	125			8	203	217
		6	663	-654			5	326	337			16	291	-287			5	362	-370			4	341	340			11	104	106
		7	201	215			6	424	422			18	343	-346			6	282	290			6	250	-247	4	7	0	99	-97
		8	618	-610			8	571	570	3	5	2	41	-40			8	231	254			8	358	-359			3	187	185
		9	66	-64			9	77	80			4	169	-181			9	125	-126			12	329	-320			5	108	-93
		10	71	-54			10	76	81			5	559	570			11	138	149			13	56	65			7	94	93
		11	158	169			11	115	-120			6	501	-506	8	5	0	83	-86	5	6	1	280	285			9	221	-221
		12	73	-91			12	87	-94			7	188	-188			1	193	199			2	44	50	5	7	1	171	179
		13	282	279			13	123	-124			8	326	-336			3	224	221			3	105	103			2	114	-117
		14	390	398	8	4	0	785	793			11	170	-185			5	125	132			4	154	149			4	94	-98
		16	179	175			1	72	-65			13	177	-178			7	108	97			5	369	378			5	233	248
		17	136	130			3	115	123			14	314	327	0	6	0	1437	-1458			6	101	-102			7	156	-162
		18	108	118			4	186	185			16	102	92			2	192	-193			7	227	-230	6	7	0	413	409
4	4	0	1540	-1496			6	80	-90			17	71	-77			4	269	-276			8	153	-156			2	67	-68
		1	83	71			8	164	-163	4	5	0	98	111			6	256	260			9	177	-176			3	80	95
		2	311	-312			10	82	72			1	177	-172			8	378	383			11	370	-368	0	8	0	695	712
		3	72	-68	9	4	1	293	305			2	99	91			10	160	179			12	140	-148			2	169	179
		4	571	-549			3	180	177			3	101	-92			12	464	470	6	6	1	234	-238			6	75	-62
		6	359	347			4	105	108			5	132	-141			14	174	184			3	399	-380			8	291	-328
		8	590	579			5	334	344			6	66	-61			16	126	124			5	191	-197	1	8	1	77	87
		9	44	-51			6	148	-143			8	58	-59	1	6	1	201	-210			7	238	-233			4	76	67
		12	533	522			7	255	-258			9	133	116			4	80	-54	7	6	2	108	-109			5	268	283
		13	106	-94	0	5	1	386	386			11	228	-223			5	449	-462			3	111	128			6	66	-86
		14	363	367			3	135	129			12	56	-45			6	173	178			4	188	-199			7	76	-85
		16	256	247			5	152	-133			13	439	-435			7	133	134			5	228	-238	2	8	1	82	-79
5	4	1	495	-485			7	123	-137			15	55	63			8	314	331			6	266	-270			3	443	-453
		3	210	-204			11	268	264	5	5	1	310	-312			9	75	76	0	7	3	216	-223			5	180	-180
		4	188	-172			13	476	465			2	167	161			10	77	83			5	283	289	3	8	3	73	55
		5	557	-559			17	203	208			3	48	-53			11	307	324			7	68	-46			4	64	-67
		6	187	191	1	5	1	327	327			4	131	118			12	124	123			9	173	170			5	250	-262
		7	336	343			2	57	29			5	377	-393			13	214	216			11	285	-294					

the mean of the two minimum F_o measured values, was attributed. The intensities were corrected for Lorentz and polarization effects. No correction for absorption was applied.

Structure determination

The systematic absences are consistent with the space groups *Pnma* or $Pna2_1$. Intensity statistic tests clearly indicated the centrosymmetric space group. As this group would require a large percentage of atoms on special position a first attempt to find a solution to the structure was made in $Pna2_1$. The multisolution technique of GERMAIN, MAIN and WOOLFSON (1971) was used, with 180 reflections having $|E| \geq 1.30$ as input. The heavy-atom locations were derived from Fourier E map obtained using the solution with the higest figure of merit. The structure-factor calculation for this partial structure yielded an isotropic $R = \Sigma||F_o| - \Sigma|F_o||/|F_o|$ of 0.22 for the observed reflections. The oxygen atoms were located from F_o synthesis but the new R index reached 0.27. The structure was then refined in *Pnma*

Table 5. *Analysis of anisotropic thermal parameters*

α, β and γ are the angles of the principal axes of the thermal ellipsoids with respect to the crystallographic axes

Atom	Root-mean-square	α	β	γ
Cu	0.120 Å	88°	90°	2°
	0.181	90	0	90
	0.108	2	90	92
K(1)	0.144	90	0	90
	0.222	86	90	4
	0.125	4	90	94
K(2)	0.141	105	90	15
	0.144	90	0	90
	0.130	15	90	75
Cl(1)	0.142	130	90	40
	0.172	90	0	90
	0.122	40	90	50
Cl(2)	0.146	90	0	90
	0.154	44	90	135
	0.120	45	90	45
S	0.122	104	90	14
	0.123	90	0	90
	0.102	14	90	75
O(1)	0.139	86	90	4
	0.209	90	0	90
	0.092	4	90	94
O(2)	0.145	56	107	39
	0.169	34	84	123
	0.100	85	18	73
O(3)	0.134	68	90	22
	0.197	90	0	90
	0.089	22	90	112

assuming that K, Cu, Cl, S and two O were on the symmetry plane. Atomic coordinates and anisotropic temperature parameters, in Tables 2 and 3 respectively, were refined by a modified version of the full-matrix least-squares program ORFLS (Busing, Martin and Levy,

Table 6. *Interatomic distances*

(with standard deviations in parentheses) in chlorotionite

Cu—Cl(1) (2×)	3.0467(2) Å	K(1)—Cl(2)	3.213 (3) Å
—Cl(1″)	2.237 (2)	—Cl(1)	3.262 (3)
—Cl(2)	2.252 (2)	—O(2′) (2×)	2.716 (5)
—O(1)	2.001 (6)	—O(2) (2×)	2.719 (5)
—O(3)	2.019 (6)		
		K(2)—Cl(2″) (2×)	3.1320(6)
S—O(1)	1.500 (6)	—O(2′) (2×)	2.828 (5)
—O(3)	1.506 (6)	—O(3)	2.853 (6)
—O(2) (2×)	1.460 (4)	—O*(1)	2.744 (6)

* indicates atoms of adjacent cells.

Table 7. *Interatomic angles in* $CuCl_4O_2$ *and in* SO_4

(with standard deviations in parentheses)

Cl(1)—Cu—Cl*(1)	171.83(6)°	Cl(2)—Cu—O(1)	94.6(2)
—Cl(1)	89.85(4)	O(1)—Cu—O(3)	70.7(2)
—Cl(2)	94.05(4)	O(1)— S —O(3)	101.3(3)
—O(1)	89.17(4)	—O(2) (2×)	112.2(2)
—O(3)	85.95(4)	O(3)— S —O(2) (2×)	111.8(2)
Cl(1)—Cu—Cl(2)	99.39(8)	O(2)— S —O(2)	111.2(3)
—O(3)	95.4(2)		

* indicates atoms of adjacent cells.

1962). The final R value is 0.032 for 893 observed reflections and 0.041 with the unobserved ones included. Observed and calculated structure factors are compared in Table 4. The analyses of the anisotropic thermal parameters are given in Table 5. Interatomic distances, angles and their standard deviations are in Tables 6 and 7.

Description of the structure

The complete atomic arrangement of chlorotionite is shown in Fig. 1. The crystal structure of chlorotionite is built up by three kinds of polyhedra: [$CuCl_4O_2$] pseudo-octahedra, SO_4 tetrahedra and KCl_2O_4 polyhedra.

Around Cu an irregular square-planar arrangement of ligand atoms occurs which involves two chlorine in *cis* position and two oxygen atoms, all placed on the mirror plane. The usual [4 + 2] coordination

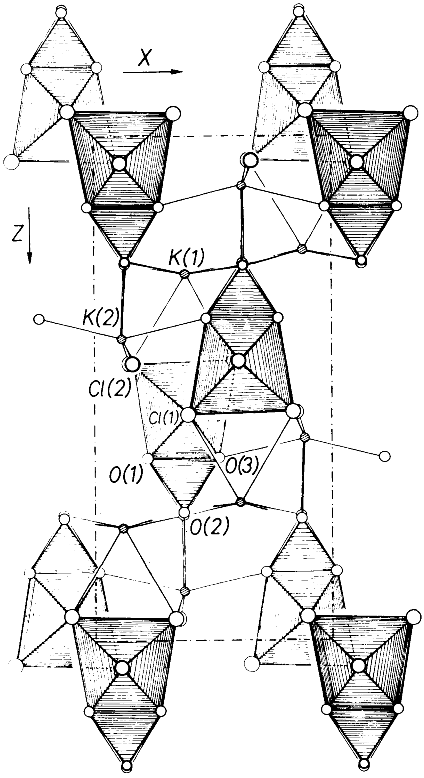

Fig. 1. Projection of the chlorotionite structure on the *xz* plane. For clarity some atoms are slightly shifted from the positions symmetrically related by mirror plane

is completed by two chlorine atoms which are the apices of the pseudo-octahedron. The two closer chlorine neighbours have distances Cu—Cl(1) and Cu—Cl(2) of 2.24 and 2.25 Å respectively and the two more distant Cu—Cl(1) [× 2] of 3.05 Å. These values can be usefully compared with those found by Dunitz (1957) in $CuPy_2Cl_2$, where each Cu has two closer chlorine atoms in *trans* configuration (2.28 Å) and two more distant (3.05 Å). As shown by Fig. 2 the metal-oxygen distances are Cu—O(1) = 2.00 Å and Cu—O(3) = 2.02 Å. It is of interest that the bond angles around the copper atom are strongly distorted (see Fig. 2 and 3). For example, O(1)—Cu—O(3) is almost 71 ° and Cl*(1)—Cu—Cl(1) is almost 172 °. This last value is significantly different from that found in caledonite (Giacovazzo, Menchetti and

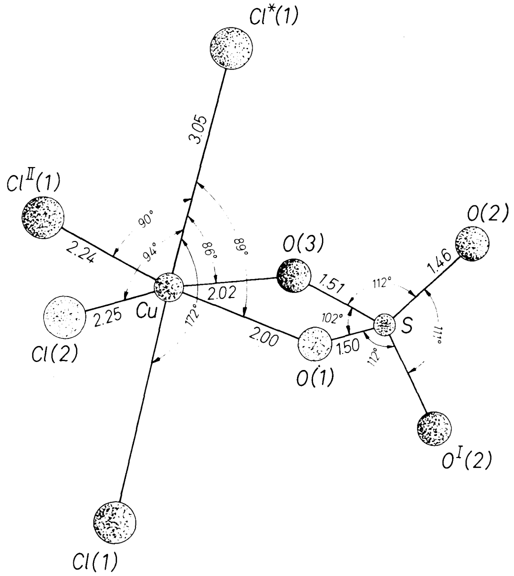

Fig. 2. Configuration and connection between $Cu[Cl_4O_2]$ and SO_4 showing some metal-anions angles and distances

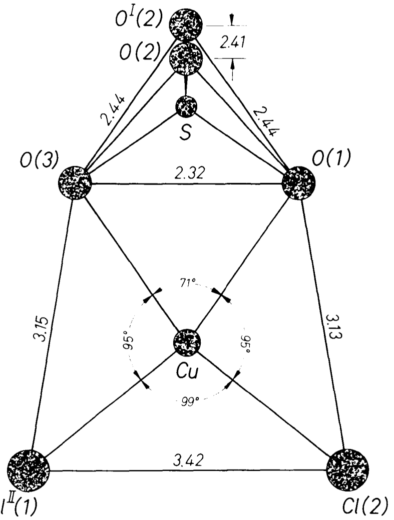

Fig. 3. The Cu—S configuration showing O—O distances and four Cu-anion angles

Scordari, 1973) and in copper dipyridine dichloride (Dunitz, 1957) which are 177° and 176° respectively.

The sulphate group shows a distorted tetrahedral configuration with two S—O(1) and S—O(3) longer distances (1.50 and 1.51 Å) and two shorter symmetry related S—O(2) ones (1.46 Å). SO_4 tetrahedra are linked by O(1)—O(3) edges with Cu pseudo-octahedra. Because of their electrostatic repulsion, S and Cu are pushed towards O(2)—O^{I}(2) and Cl^{II}(1)—Cl(2) edges respectively. Consequently O(1)—O(3) is the smallest (2.32 Å) of the O—O distances in the SO_4 tetrahedron against an average value of 2.43 Å, and O(1)—S—O(3) is the smallest angle (about 102°) against an average value of 112°. The electrostatic repulsion Cu—S and the steric effect due to two bulky Cl atoms in *cis* position seem to cause the above-mentioned distortion occuring in the Cu pseudo-octahedra.

In chlorotionite there are two symmetrically independent potassium atoms K(1) and K(2) lying on the mirror plane. Both K(1) and K(2) are surrounded by four oxygen and two chlorine atoms, but the coordination polyhedra are rather different: K(1) has four K(1)—O(2) distances of 2.71 Å and two K(1)—Cl with a mean value of 3.24 Å. It lies at the top of a four-sided pyramid, whose basis is made by four oxygen atoms; two additional chlorine atoms complete the environement. The resultant polyhedron is similar to a trigonal prism.

K(2) has three K(2)—O distances with a mean value of 2.84 Å, one K(1)—O(1) of 2.74 Å, and two K(2)—Cl(2) of 3.13 Å. These six anions form a polyhedron similar to a distorted pseudo-octahedron. K(2) is much more influenced by the S-electrostatic repulsion than K(1). In fact, K(2)—O distances are in the average larger than K(1)—O and K(2)—Cl shorter than K(1)—Cl.

The most interesting structural features in chlorotionite are chains running along the *b* axis: $Cu[Cl_2,O_2]Cl_2$ pseudo-octahedra are connected via Cl(1) apices to form a straight chain. Two of these chains, shifted against each other by $\frac{1}{2}$ *b* are joined by common zigzag Cl(1)—Cl(1) edges to form a compact double chain (see Fig. 4) whose repeat unit is $^{\infty}_{1}[Cu_2Cl_4O_4(SO_4)_2]^{12-}$. SO_4 tetrahedra are linked on opposite sides to Cu pseudo-octahedra by O(1)—O(3) edges. They constitude a "head-bridge" towards parallel Cu chains (Fig. 1). The double chains are connected by K polyhedra.

As well known, Cu pseudo-octahedra frequently form simple chains as in natrochalcite (Rumanova and Volodina, 1958), in caledonite (Giacovazzo, Menchetti and Scordari, 1973), in linarite (Bachmann and Zemann, 1961) etc., or sheets as in brochantite (Cocco e Mazzi, 1959), in dolerophanite (Flügel-Kahler, 1963), or three-dimensional networks as in cornetite (Fehlmann *et al.*, 1964). This structure therefore reveals a rather unusual crystallochemical feature of Cu pseudo-octahedra.

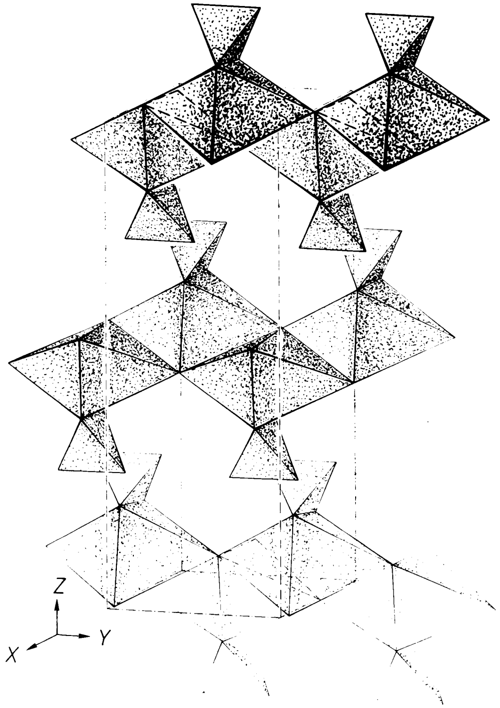

Fig. 4. Partial clinographic projection of chlorotionite. Cu pseudo-octahedra are linked forming chains parallel to the *b* axis

Considering physical properties of chlorotionite, the structure explains

a) the prismatic habit elongated in [010] direction. The direction of the Cu chains coincides in fact with *b*.

b) the easy cleavage on {100}, {101}, {001}. The cleavage planes {100} and {001} were already noticed by Bellanca (1946) together with a {010} easy cleavage plane. However, the structure does not explain this last one.

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References

H. G. BACHMANN und J. ZEMANN (1961), Die Kristallstruktur von Linarit, $PbCuSO_4(OH)_2$. Acta Crystallogr. **14**, 747—753.

A. BELLANCA (1946). Cella elementare e gruppo spaziale della clorotionite. Periodico Min. **15**, 33—41.

W. R. BUSING, K. O. MARTIN and H. A. LEVY (1962), ORFLS. 2nd edit. Oak Ridge National Laboratory Report ORNL-TM-305.

G. COCCO e F. MAZZI (1959), La struttura della brochantite. Periodico Min. **28**, 121—149.

J. D. DUNITZ (1957), The crystal structures of copper dipyridine dichloride and the violet form of cobalt dipyridine dichloride. Acta Crystallogr. **10**, 307—313.

M. FEHLMANN, S. GHOSE and J. J. FINNEY (1964), Direct determination of the crystal structure of cornetite, $Cu_3PO_4(OH)_3$, by the Monte Carlo Method. J. Chem. Physics **41**, 1910—1916.

E. FLÜGEL-KAHLER (1963), Die Kristallstruktur von Dolerophanit, $Cu_2O(SO_4)$. Acta Crystallogr. **16**, 1009—1014.

G. GERMAIN, P. MAIN and M. M. WOOLFSON (1971), The application of phase relations to complex structures. III. The optimum use of phase relationships. Acta Crystallogr. A **27**, 368—376.

C. GIACOVAZZO, S. MENCHETTI and F. SCORDARI (1973), The crystal structure of caledonite, $Cu_2Pb_5(SO_4)_3CO_3(OH)_6$. Acta Crystallogr. B **29**, 1986—1990.

W. C. HAMILTON (1959), On the isotropic temperature factor equivalent to a given anisotropic temperature factor. Acta Crystallogr. **12**, 609—610.

I. M. RUMANOVA and G. F. VOLODINA (1958), *From crystal chemical classification of minerals.* 2nd edit. by A. S. POVARENNYKH, Plenum Press, New York, 1972.

A. SCACCHI (1872). From A. BELLANCA (1946), Periodico Min. **15**, 33—41.

F. ZAMBONINI (1935). From A. BELLANCA (1946), Periodico Min. **15**, 33—41.