

## The halotrichite group: the crystal structure of apjohnite

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**SUMMARY.** Apjohnite,  $\text{MnAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$ , is monoclinic, space group  $P2_1/c$ ,  $a$  6.198 (2),  $b$  24.347 (4),  $c$  21.266 (4) Å,  $\beta$  100.28 (3)° and  $Z = 4$ . The crystal structure was determined by means of direct methods applied to X-ray data collected with a single-crystal diffractometer. At the end of the refinement, performed with least-squares method, the  $R$  index was 0.039.

The  $\text{SO}_4$  tetrahedra,  $\text{Al}(\text{H}_2\text{O})_6$  octahedra, and  $\text{MnO}(\text{H}_2\text{O})_6$  octahedra are connected by a hydrogen bonding system; the only direct connection between polyhedra is by sharing of an oxygen between  $\text{S}(4)$  and  $\text{Mn}$ . In the asymmetric unit there are twenty-two water molecules, five of which lie in channels of the structure and are not linked to the cations but only to ligand water oxygens by means of hydrogen bonds.

Powder data indicate a close structural relationship between apjohnite, halotrichite, and pickeringite.

THE halotrichite group comprises a series of minerals that present a good example of isomorphic substitutions. The general formula can be written  $AB_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$ , where  $A$  is mainly  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$  while  $B$  is  $\text{Al}^{3+}$  (subordinately  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$ ). Several analyses support the existence of a complete series between the  $\text{Fe}^{2+}$  end-member (halotrichite) and the  $\text{Mg}^{2+}$  analogue (pickeringite). It is likely that the series extends also towards the  $\text{Mn}^{2+}$  end-member (apjohnite).

A morphological and X-ray study on pickeringite and halotrichite was performed by Bandy (1938), who reported for pickeringite the space group  $P2/m$ ; morphological study by Gordon (1942) indicated sphenoidal symmetry, so that in Dana's System (Palache *et al.*, 1951) the space group is given as  $P2$ .

The crystal structure determination presented some difficulties because of the unusually high number of atoms (89) in the asymmetric unit and because of the thin hair-like shape of the crystals. The present investigation, dealing with the crystal structure of apjohnite, forms a part of a series of crystal-chemical studies on hydrated sulphate minerals.

*Experimental.* Many acicular crystals of pickeringite from Vulcano, from Vesuvius, and from Elba were examined together with some halotrichite crystals, but they were invariably found to be too thin to give reliable intensity data. Crystals suitable for the X-ray study were found only on a sample of apjohnite from Terlano, Bolzano, Italy, kindly supplied by the Revd. Tullio Stolcis.

A partial chemical analysis of this sample was performed by Dr. A. Bencini by atomic absorption. The results for Mn, Mg, Zn, and Fe yield the formula:  $(\text{Mn}_{0.64}, \text{Mg}_{0.28}, \text{Zn}_{0.06}, \text{Fe}_{0.02}) \text{Al}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$ . Two different samples from the same locality

were previously studied by Meixner and Pillewizer (1937), who found one to be a manganoan pickeringite and the other a magnesian apjohnite. Unfortunately Pillewizer's A analysis is not fully reliable because of the noticeable amount (*c.* 25 %) of admixed epsomite; however, after deducting this one can evaluate an atomic ratio Mn/Mg of 1.2, while the B sample gives a ratio of 0.26. The value found in the present study (Mn/Mg = 2.29) together with the two previous ones, indicates a large diadochy between the two cations.

TABLE I. *X-ray powder pattern of apjohnite. Philips diffractometer, Ni-filtered Cu-K $\alpha$  radiation, internal NaF standard*

<i>hkl</i>	<i>d</i> <sub>calc</sub>	<i>d</i> <sub>obs</sub>	<i>I</i>	<i>hkl</i>	<i>d</i> <sub>calc</sub>	<i>d</i> <sub>obs</sub>	<i>I</i>	<i>hkl</i>	<i>d</i> <sub>calc</sub>	<i>d</i> <sub>obs</sub>	<i>I</i>
	Å	Å			Å	Å			Å	Å	
002	10.462	10.55	10	063	3.507	3.515	100	174	2.723	2.726	5
021	10.522			124	3.506			222	2.726		
012	9.612	9.65	10	016	3.452	3.454	11	182	2.688	2.689	19
022	7.935	7.96	10	026	3.353	3.361	8	232	2.644	2.650	1
023	6.052	6.07	20	134	3.337	3.346		213	2.612	2.617	10
041	5.845	5.85	5	072	3.301	3.306	4			2.583	1
121	5.495	5.48	5	162	3.312			2.563	12		
033	5.290	5.29	8	161	3.283	3.294	4			2.524	4
042	5.261			116	3.261	3.268	3	2.465	8B		
113	4.954	4.97	18	145	3.211	3.212	3			2.408	9
130	4.875	4.88	5	126	3.177	3.175	10			2.288	4
024	4.806	4.82	90	163	3.166			2.258	1		
123	4.673	4.69	5	073	3.113	3.119	2			2.239	6
131	4.605	4.61	6	202	3.079	3.080	2			2.199	3
122	4.547	4.55	3	211	3.073			2.168	2		
052	4.415	4.41	6	136	3.050	3.055	9			2.133	4
104	4.375	4.38		210	3.026	3.032	5				2.087
141	4.329	4.34	27	046	3.026			2.064	3B		
140	4.308	4.32		164	2.975	2.051	3B				
142	4.173	4.18	12	213	2.975	2.974	15			2.020	13
113	4.170			017	2.967			1.977	4		
124	4.117	4.13	22	146	2.895	2.901	11			1.960	6
141	4.118			214	2.847	1.896	5				
123	3.997	4.008	10	172	2.837	2.840	12			1.879	12B
025	3.958	3.967	23	056	2.835			1.866	8		
143	3.891	3.902	6	224	2.790	2.793	11			1.840	2B
062	3.783	3.792	33	202	2.797			1.827	3		
151	3.673	3.676	4	083	2.789	2.789	4			1.784	4B
104	3.661	3.667		212	2.778			1.715	4		
114	3.620	3.625	6	231	2.767	2.769	6				
				165	2.766						

The powder pattern of apjohnite is reported in Table I; it was partially indexed on the basis of the unit-cell dimensions obtained from a single crystal and taking into account the intensities as measured on a single-crystal diffractometer. By comparison of Table I with the JCPDS cards 11-506 and 12-299 (JCPDS, 1971) the close structural relationship between apjohnite, halotrichite, and pickeringite is evident. The unit cell dimensions were determined from twenty-five high theta reflections measured on a single-crystal diffractometer: *a* 6.198 (2), *b* 24.347 (4), *c* 21.266 (4) Å, and  $\beta$  100.28 (3)°. The observed density, determined by the flotation method, is 1.81 g cm<sup>-3</sup> and the

calculated value is  $1.836 \text{ g cm}^{-3}$ . The space group, uniquely determined from the systematic absences, is  $P2_1/c$ . The transformation matrix from Bandy's (1938) orientation to the one of the present study is  $001/010/\bar{1}0\bar{1}$ .

Intensities were collected with a Philips PW 1100 4-circle computer-controlled diffractometer (Centro di Cristallografia Strutturale del CNR, Pavia, Italy), with Cu- $K\alpha$  radiation and the  $\omega$ - $2\theta$  scan technique. A total of 3349 independent reflections in the range  $2^\circ < \theta < 50^\circ$  were measured with scan speed  $0.025^\circ/\text{sec}$  and scan range  $1.0^\circ$ ; only 2423 reflections were judged to be actually measured according to the criterion  $I \geq 3\sigma(I)$ . Intensities were corrected for Lorentz-polarization effects, while absorption correction was considered negligible because the crystal was so thin.

*Structure determination and refinement.* The structure was solved by means of direct methods using the MULTAN computer program (Germain, Main, and Woolfson, 1971). In spite of the high number of atoms in the asymmetric unit, MULTAN was able to supply automatically the correct solution, working on 400 normalized structure amplitudes with  $E \geq 1.55$ . The Fourier synthesis computed from the phasing of these 400 structure factors gave clear indications on all atoms but five oxygens, and of course the hydrogen atoms. The  $R$  index (defined as  $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ ) was 0.32. In the next electron density map the missing oxygen atoms were located.

The refinement of the structure was performed by the least-squares method; all observed reflections were assigned a weight  $1/\sqrt{\sigma}$  with  $\sigma$  deriving from counting statistics. Thermal parameters, at first individual isotropic and later anisotropic, were allowed to vary. Towards the end of the refinement a difference Fourier synthesis was computed in order to locate the hydrogen atoms. Sufficiently reliable indications were obtained for thirty-two hydrogens, which were subsequently refined with a thermal parameter fixed at  $7.5 \text{ \AA}^2$ . The twelve missing hydrogen atoms were located taking into account the consistency of the general hydrogen-bonding system; their positional parameters were computed assuming that H atoms lie approximately on the donor-acceptor alignment about one-third of the donor-acceptor distance from the donor. These latter twelve atoms were not refined. With the atom parameters given in Tables II and III and taking into account the anomalous dispersion correction for the divalent cation (Cromer and Liberman, 1970) the final  $R$  index was 0.039 for all observed reflections and 0.059 including the unobserved ones. The atomic scattering factors for neutral atoms were obtained by interpolation of the values given by Cromer and Waber (1965); for hydrogen atoms the values given by Stewart, Davidson, and Simpson (1965) were used. A table of observed and calculated structure factors is deposited in the library of the Department of Mineralogy, British Museum (Natural History).

*Discussion.* As one can evaluate from the high number of water molecules in the chemical formula, the hydrogen-bonding system is of particular relevance in this structure. In fact the three-dimensional connection in apjohnite is really due to bonds of this kind, in the same way as in the structure of alunogen (Menchetti and Sabelli, 1974). Since the ratio between the number of water molecules (22) and cations (3) exceeds the oxygen coordination of the cations (C.N. = 6) one can conclude that at least four water molecules cannot behave as ligands. Actually in apjohnite there are seventeen ligand water molecules and five 'free' water molecules. This is due to the

TABLE II. Positional parameters, thermal parameters ( $\times 10^5$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2$ ) according to Hamilton. The anisotropic temperature factors are in the form

$$T = \exp\{- (h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$$

	$x/a$	$y/b$	$z/c$	$B_{eq.}$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Mn	0.36995(17)	0.59600(4)	0.08053(5)	1.09	757(35)	40(2)	64(3)	-18(8)	2(8)	-5(2)
Al(1)	0.44015(29)	0.61206(7)	0.42426(8)	1.29	892(58)	46(4)	78(5)	-21(12)	3(13)	4(3)
Al(2)	0.68079(28)	0.34315(7)	0.19779(8)	1.24	937(59)	47(4)	67(5)	11(12)	26(13)	-3(4)
S(1)	0.08662(25)	0.24404(6)	0.52658(7)	1.45	985(52)	53(3)	90(4)	-15(11)	16(12)	-2(3)
S(2)	0.96419(24)	0.46510(6)	0.38825(7)	1.32	972(50)	51(3)	71(4)	-24(10)	24(11)	-2(3)
S(3)	0.14189(24)	0.19411(6)	0.25596(7)	1.49	1099(53)	63(3)	76(4)	55(11)	52(12)	11(3)
S(4)	0.16025(25)	0.47277(6)	0.10454(7)	1.59	1214(54)	61(3)	81(4)	-52(11)	11(12)	10(3)
O(1)	0.1310(6)	0.2170(2)	0.4679(2)	2.81	2080(154)	111(9)	166(13)	-49(30)	212(36)	-58(9)
O(2)	0.0271(6)	0.3022(1)	0.5126(2)	2.23	1399(140)	61(9)	175(12)	7(30)	45(32)	9(8)
O(3)	0.0941(6)	0.2154(2)	0.5490(2)	2.47	1751(147)	117(9)	118(12)	-110(30)	119(34)	10(9)
O(4)	0.2866(6)	0.2426(2)	0.5763(2)	2.75	1602(152)	96(9)	177(13)	19(31)	-164(35)	7(9)
O(5)	1.0118(6)	0.4371(2)	0.3311(2)	2.40	1640(146)	100(9)	137(12)	13(30)	87(33)	-48(9)
O(6)	0.9042(6)	0.5228(1)	0.3727(2)	2.21	1487(141)	66(9)	155(12)	57(29)	13(32)	15(8)
O(7)	1.1656(6)	0.4644(2)	0.4380(2)	2.51	1799(150)	83(9)	131(12)	-68(29)	-220(33)	27(9)
O(8)	0.7860(6)	0.4360(2)	0.4119(2)	2.83	1966(155)	132(10)	144(13)	-176(31)	150(35)	2(9)
O(9)	0.1249(6)	0.1833(2)	0.3228(2)	3.20	2901(170)	149(10)	110(12)	215(34)	214(35)	42(9)
O(10)	0.2217(6)	0.2505(2)	0.2490(2)	2.58	1528(144)	73(8)	204(13)	-83(29)	28(35)	14(9)
O(11)	0.0809(6)	0.1890(2)	0.2155(2)	2.67	1456(147)	116(10)	167(13)	18(30)	3(34)	-28(9)
O(12)	0.2933(6)	0.1541(2)	0.2342(2)	2.56	2066(150)	108(9)	124(12)	258(31)	160(33)	28(9)
O(13)	0.1610(6)	0.4437(2)	0.1659(2)	2.74	1670(146)	127(10)	162(13)	144(30)	146(34)	80(9)
O(14)	0.2279(7)	0.4341(2)	0.0593(2)	3.65	2299(164)	195(11)	177(13)	-94(35)	225(37)	-79(10)
O(15)	0.0616(6)	0.4935(2)	0.0801(2)	2.97	1825(156)	128(10)	162(13)	-16(32)	-64(36)	23(9)
O(16)	0.3170(6)	0.5185(2)	0.1176(2)	3.24	2004(160)	86(10)	231(14)	-226(31)	-216(37)	32(9)
O(17)	0.7097(6)	0.5854(1)	0.1272(2)	2.47	1574(144)	102(9)	153(12)	23(29)	99(33)	-15(9)
O(18)	0.3275(6)	0.6323(2)	0.1728(2)	2.93	1406(143)	150(10)	173(13)	72(31)	47(33)	-48(9)
O(19)	0.4493(6)	0.6756(2)	0.0437(2)	3.17	1743(147)	121(10)	207(13)	-142(31)	-103(35)	46(9)
O(20)	0.0329(6)	0.6122(2)	0.0451(2)	2.30	1618(144)	101(9)	119(12)	8(29)	73(33)	-20(9)

TABLE II (cont.)

	$x/a$	$y/b$	$z/c$	$B_{\text{eq}}$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
O(21)	0.4004(7)	0.5611(2)	—	4.82	2371(191)	241(12)	304(16)	-114(39)	205(44)	-99(12)
O(22)	0.4974(6)	0.5572(1)	0.3680(2)	2.02	1255(136)	88(8)	117(11)	-9(28)	40(31)	-10(8)
O(23)	0.1491(6)	0.6181(1)	0.3781(2)	1.84	971(130)	69(8)	132(12)	-11(26)	4(30)	12(8)
O(24)	0.5339(6)	0.6666(1)	0.3724(2)	1.89	1434(133)	69(8)	103(11)	-23(27)	38(30)	4(8)
O(25)	0.3746(6)	0.6674(1)	0.4798(2)	2.11	1164(133)	88(9)	143(12)	33(27)	72(31)	-28(8)
O(26)	0.7283(6)	0.6076(1)	0.4709(2)	1.79	1285(131)	72(8)	92(11)	-38(27)	-11(30)	12(8)
O(27)	0.3524(6)	0.5570(1)	0.4763(2)	1.99	1765(140)	72(8)	94(11)	-92(28)	90(31)	2(8)
O(28)	0.5345(6)	0.3423(1)	0.1120(2)	1.98	1460(135)	82(8)	92(11)	25(28)	-68(31)	4(8)
O(29)	0.9393(6)	0.3164(1)	0.1698(2)	1.98	1346(134)	85(9)	109(11)	63(27)	-68(31)	4(8)
O(30)	0.6010(6)	0.2698(1)	0.2096(2)	1.88	1216(137)	74(8)	113(11)	6(27)	24(31)	6(8)
O(31)	0.8392(6)	0.3437(1)	0.2828(2)	2.21	1645(141)	91(9)	109(12)	15(29)	21(32)	-1(9)
O(32)	0.4301(6)	0.3678(1)	0.2238(2)	1.89	1218(134)	90(9)	104(11)	79(28)	122(30)	2(8)
O(33)	0.7696(6)	0.4155(1)	0.1850(2)	2.14	1549(140)	74(9)	133(12)	-24(28)	64(32)	2(8)
O(34)	0.8038(7)	0.2629(2)	0.3618(2)	5.64	5442(212)	226(13)	205(17)	337(41)	269(47)	36(12)
O(35)	0.2122(7)	0.5394(2)	0.2608(2)	4.45	3324(192)	206(11)	197(15)	-126(38)	111(42)	-34(11)
O(36)	0.6806(6)	0.5091(2)	0.2345(2)	3.53	2919(164)	128(10)	175(14)	126(33)	55(37)	8(10)
O(37)	0.4190(6)	0.3913(2)	0.3425(2)	3.22	1942(151)	163(10)	168(13)	51(32)	117(35)	-32(10)
O(38)	0.4073(7)	0.2954(2)	0.4097(2)	4.38	3362(181)	196(12)	183(14)	-75(38)	-4(40)	1(10)

absence of water oxygens shared between polyhedra and to the presence of one oxygen, namely O(16), that is linked to both S(4) and Mn, so making the only direct connection between polyhedra.

Each of the ligand water oxygens acts as proton donor towards sulphate oxygens or towards sulphate and free water oxygens. Donor-acceptor distances involved in these latter bonds (that is ligand water  $\rightarrow$  free water) range from 2.60 to 2.66 Å so that the free water molecules are to be considered connected strongly enough to the whole

TABLE III. *Positional parameters of H atoms*

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>		<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
H(1)	0.781(9)	0.620(2)	0.142(3)	H(23)	0.45	0.31	0.10
H(2)	0.793(9)	0.561(2)	0.112(3)	H(24)	0.43	0.37	0.09
H(3)	0.210(9)	0.647(2)	0.173(3)	H(25)	0.913(9)	0.310(2)	0.120(3)
H(4)	0.442(9)	0.643(2)	0.196(3)	H(26)	1.048(9)	0.293(2)	0.197(3)
H(5)	0.58	0.69	0.04	H(27)	0.474(9)	0.266(2)	0.226(3)
H(6)	0.32	0.69	0.01	H(28)	0.711(9)	0.248(2)	0.211(3)
H(7)	—0.015(9)	0.651(2)	0.040(3)	H(29)	0.888(9)	0.381(2)	0.303(3)
H(8)	—0.029(9)	0.593(2)	0.008(3)	H(30)	0.83	0.31	0.31
H(9)	0.52	0.56	—0.03	H(31)	0.442(9)	0.379(2)	0.260(3)
H(10)	0.29	0.54	—0.03	H(32)	0.332(9)	0.398(2)	0.195(3)
H(11)	0.632(9)	0.543(2)	0.380(3)	H(33)	0.718(9)	0.455(2)	0.209(3)
H(12)	0.421(9)	0.548(2)	0.329(3)	H(34)	0.92	0.43	0.19
H(13)	0.068(9)	0.585(2)	0.377(3)	H(35)	0.732(9)	0.262(2)	0.326(3)
H(14)	0.137(9)	0.644(2)	0.346(3)	H(36)	0.953(9)	0.232(2)	0.366(3)
H(15)	0.608(9)	0.703(2)	0.399(3)	H(37)	0.214(9)	0.570(2)	0.235(3)
H(16)	0.607(9)	0.658(2)	0.348(3)	H(38)	0.19	0.51	0.23
H(17)	0.225(9)	0.679(2)	0.476(3)	H(39)	0.69	0.54	0.20
H(18)	0.491(9)	0.690(2)	0.521(3)	H(40)	0.75	0.51	0.28
H(19)	0.828(9)	0.641(2)	0.483(3)	H(41)	0.547(9)	0.412(2)	0.361(3)
H(20)	0.764(9)	0.585(2)	0.510(3)	H(42)	0.292(9)	0.417(2)	0.338(3)
H(21)	0.307(9)	0.519(2)	0.460(2)	H(43)	0.506(9)	0.280(2)	0.385(3)
H(22)	0.302(9)	0.563(2)	0.510(3)	H(44)	0.41	0.33	0.39

structural arrangement. These free water molecules lie in channels, with an hexagonal outline (see fig. 1), running parallel to [100]; these channels are built up by the mutual arrangement of three octahedra and three tetrahedra. This feature is similar to that already observed in the structure of alunogen (Menchetti and Sabelli, 1974). The weak H bonds donated by the free molecules are directed towards oxygen atoms facing the channel, except for the two bonds in which O(38) is the donor; this atom indeed is bound to two free water molecules. All distances and angles involving hydrogen atoms are shown in Table IV.

The general hydrogen bonding system, however, is not without uncertainties: for instance the configuration of hydrogen atoms around O(34) is questionable. Within the limit of 3.30 Å, O(34) has five surrounding oxygen atoms. Two of these, namely O(31) and O(38), are likely to act as proton donors towards O(34). The other three, O(1), O(9), and O(30), are respectively 2.97, 3.00, and 3.26 Å from O(34). On the basis of the above values one could postulate the bonds O(1) . . . H—O(34)—H . . . O(9); but

the O(1)–O(34)–O(9) angle ( $64^\circ$ ) is very distant from the theoretical water angle. The O(9)–O(34)–O(30) angle instead is  $85^\circ$ ; it fits better the acceptor–donor–acceptor configuration. Two more considerations, unfortunately contradictory, are to be taken into account: in the difference Fourier map there is no positive area in the position expected for a hydrogen bridging O(34) to O(1); an opposite indication is supplied by the charge balance (see Table V) which shows O(1) to be underbonded and O(30) to be overbonded.

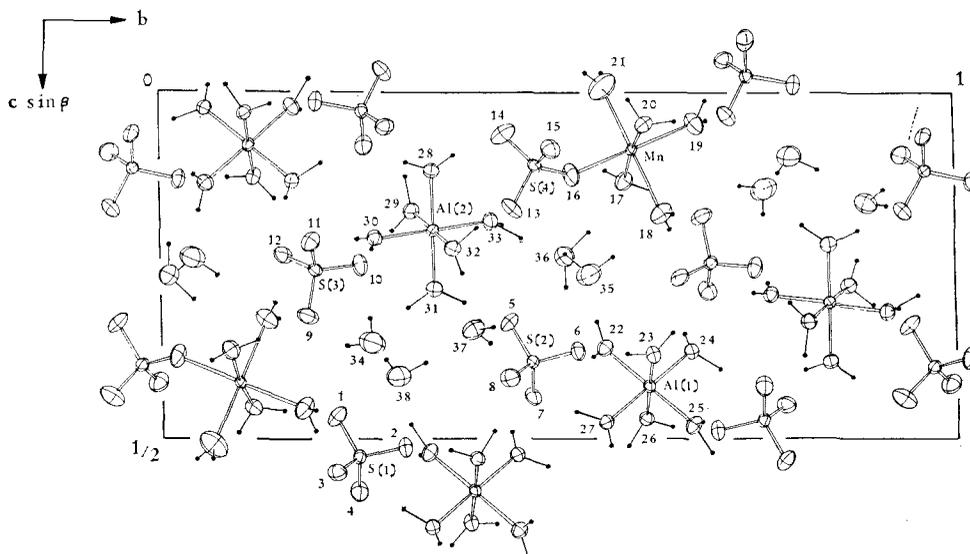


FIG. 1. Projection of the structure viewed along the  $a$ -axis.

As mentioned above, the two independent Al atoms are both coordinated by six water oxygens, while Mn is co-ordinated by five water oxygens and one sulphate oxygen. Examination of bond angles and bond lengths, reported in Tables VI and VII, shows that the three octahedra are almost regular. Within the standard deviation limits, the mean Al–O distance,  $1.884 \text{ \AA}$ , is identical to the value of  $1.882 \text{ \AA}$  found in the structure of alunogen (Menchetti and Sabelli, 1974). In the *International Tables for X-ray Crystallography* (1962), the mean value of  $1.91 \text{ \AA}$  for the Al–O distance is reported. In the Mn octahedron the Mn–O distance,  $2.093 \text{ \AA}$ , is noticeably shorter than the mean Mn–O<sub>w</sub> distance of  $2.164 \text{ \AA}$ . In the *International Tables* the mean value for the Mn–O distance is given as  $2.21 \text{ \AA}$ ; a similar value,  $2.206 \text{ \AA}$ , was found in the structure of hureaulite (Menchetti and Sabelli, 1973) where no sharp distinction between Mn–O and Mn–O<sub>w</sub> distances is present. The shorter values found in apjohnite are to be related to the presence of Mg<sup>2+</sup> substituting for Mn<sup>2+</sup>, while in hureaulite a substitution of Fe<sup>2+</sup> for Mn<sup>2+</sup> was found.

No unusual feature is shown by the four independent SO<sub>4</sub> tetrahedra for which a mean S–O bond length of  $1.476 \text{ \AA}$  was found. No lengthening of the S(4)–O(16)

TABLE IV. Distances and angles involving hydrogen atoms. The second numbering refers to the symmetry operations

A	B	C	D	E	A-B	B-C	A-C	C-D	D-E	C-E	BCD	ACE	ABC	CDE
O(9, 8)	-H(1)	-O(17)	-H(2)	-O(15, 1)	1.78 Å	0.97 Å	2.733(5) Å	0.89 Å	2.04 Å	2.919(6) Å	115°	129.1(2)°	169°	168°
O(9, 9)	-H(3)	-O(18)	-H(4)	-O(12, 8)	2.27	0.81	3.083(6)	0.83	2.02	2.839(5)	122	123.2(2)	177	167
O(1, 8)	-H(5)	-O(19)	-H(6)	-O(3, 9)	1.94	0.95	2.892(6)	1.00	1.81	2.812(5)	113	114.7(2)	178	178
O(1, 9)	-H(7)	-O(20)	-H(8)	-O(14, 7)	1.76	0.98	2.742(5)	0.93	1.85	2.745(5)	108	98.4(2)	174	164
O(14, 5)	-H(9)	-O(21)	-H(10)	-O(15, 7)	1.79	0.92	2.699(7)	0.90	1.81	2.699(6)	112	116.1(2)	171	171
O(6)	-H(11)	-O(22)	-H(12)	-O(35)	1.79	0.90	2.642(5)	0.90	1.78	2.657(5)	118	117.7(2)	157	164
O(6, 2)	-H(13)	-O(23)	-H(14)	-O(11, 9)	1.82	0.94	2.763(5)	0.92	1.70	2.612(5)	126	120.7(2)	178	173
O(4, 4)	-H(15)	-O(24)	-H(16)	-O(12, 8)	1.54	1.10	2.625(5)	0.77	1.96	2.692(5)	108	104.0(2)	170	158
O(2, 6)	-H(17)	-O(25)	-H(18)	-O(38, 4)	1.69	0.96	2.630(5)	1.16	1.55	2.652(5)	113	100.8(2)	167	157
O(2, 4)	-H(19)	-O(26)	-H(20)	-O(7, 3)	1.65	1.02	2.656(5)	1.00	1.63	2.610(5)	101	113.3(2)	168	165
O(7, 2)	-H(21)	-O(27)	-H(22)	-O(8, 4)	1.62	1.01	2.597(5)	0.86	1.83	2.672(6)	108	97.9(2)	163	170
O(4, 11)	-H(23)	-O(28)	-H(24)	-O(14)	1.65	0.95	2.605(5)	0.99	2.03	3.017(5)	99	100.3(2)	175	170
O(3, 10)	-H(25)	-O(29)	-H(26)	-O(10, 1)	1.63	1.05	2.656(5)	0.99	1.74	2.723(5)	118	110.9(2)	165	175
O(10)	-H(27)	-O(30)	-H(28)	-O(11, 1)	1.76	0.92	2.673(6)	0.87	1.91	2.771(5)	130	121.3(2)	173	170
O(5)	-H(29)	-O(31)	-H(30)	-O(34)	1.64	1.02	2.643(5)	1.01	1.62	2.620(6)	121	118.1(2)	169	171
O(37)	-H(31)	-O(32)	-H(32)	-O(13)	1.80	0.82	2.599(5)	1.08	1.58	2.640(5)	106	100.1(2)	166	167
O(36)	-H(33)	-O(33)	-H(34)	-O(13, 1)	1.47	1.15	2.607(6)	0.98	1.70	2.621(6)	89	95.9(2)	171	155
O(30)	-H(35)	-O(34)	-H(36)	-O(9, 1)	2.47	0.81	3.259(5)	1.19	1.93	2.999(6)	110	85.2(2)	165	147
O(18)	-H(37)	-O(35)	-H(38)	-O(13)	2.21	0.93	3.099(6)	0.96	2.10	3.062(6)	103	99.5(2)	161	176
O(17)	-H(39)	-O(36)	-H(40)	-O(6)	1.93	1.06	2.973(6)	0.99	2.06	3.036(5)	126	126.5(2)	170	172
O(8)	-H(41)	-O(37)	-H(42)	-O(5, 2)	1.76	0.97	2.709(5)	0.99	1.79	2.730(6)	107	123.8(2)	164	158
O(34)	-H(43)	-O(38)	-H(44)	-O(37)	2.04	0.95	2.932(7)	0.94	1.81	2.745(6)	92	87.0(2)	157	172

Symmetry code:

none	x	y	z	3	2-x	1-y	1-z	6	-x	1-y	1-z	9	-x	1/2+y	1/2-z
1	1+x	y	z	4	1-x	1-y	1-z	7	-x	1-y	1-z	10	1+x	1/2-y	z-1/2
2	x-1	y	z	5	1-x	1-y	-z	8	1-x	1/2+y	1/2-z	11	x	1/2-y	z-1/2

TABLE V. *Electrostatic balance*

	Mn	S	H-	... H	Total		Mn	S	H-	... H	Total
	Al						Al				
O(1)	—	1·49	—	0·37	1·86	O(20)	0·35	—	1·60	—	1·95
O(2)	—	1·49	—	0·46	1·95	O(21)	0·34	—	1·56	—	1·90
O(3)	—	1·53	—	0·41	1·94	O(22)	0·52	—	1·53	—	2·05
O(4)	—	1·49	—	0·49	1·98	O(23)	0·48	—	1·55	—	2·03
O(5)	—	1·53	—	0·44	1·97	O(24)	0·50	—	1·54	—	2·04
O(6)	—	1·50	—	0·58	2·08	O(25)	0·50	—	1·54	—	2·04
O(7)	—	1·46	—	0·50	1·96	O(26)	0·50	—	1·53	—	2·03
O(8)	—	1·51	—	0·45	1·96	O(27)	0·50	—	1·51	—	2·01
O(9)	—	1·55	—	0·49	2·04	O(28)	0·48	—	1·61	—	2·09
O(10)	—	1·52	—	0·44	1·96	O(29)	0·50	—	1·56	—	2·06
O(11)	—	1·44	—	0·44	1·88	O(30)	0·49	—	1·58	0·12	2·19
O(12)	—	1·49	—	0·40	1·89	O(31)	0·50	—	1·54	—	2·04
O(13)	—	1·45	—	0·61	2·06	O(32)	0·51	—	1·52	—	2·03
O(14)	—	1·55	—	0·56	2·11	O(33)	0·52	—	1·51	—	2·03
O(15)	—	1·50	—	0·38	1·88	O(34)	—	—	1·73	0·39	2·12
O(16)	0·39	1·50	—	—	1·89	O(35)	—	—	1·73	0·23	1·96
O(17)	0·31	—	1·63	0·15	2·09	O(36)	—	—	1·71	0·25	1·96
O(18)	0·29	—	1·69	0·13	2·11	O(37)	—	—	1·57	0·45	2·02
O(19)	0·32	—	1·65	—	1·97	O(38)	—	—	1·64	0·23	1·87

TABLE VI. *Bond distances*

S (1)- O (1) 1·480 (4) Å	S (3)- O (9) 1·468 (4) Å	Mn- O (16) 2·093 (4) Å	Al (2)-O (28) 1·899 (4)
O (2) 1·479 (4)	O (10) 1·476 (4)	O (17) 2·177 (4)	O (29) 1·887 (4)
O (3) 1·469 (4)	O (11) 1·497 (4)	O (18) 2·209 (4)	O (30) 1·894 (4)
O (4) 1·479 (4)	O (12) 1·482 (4)	O (19) 2·165 (4)	O (31) 1·885 (4)
S (2)- O (5) 1·468 (4)	S (4)- O (13) 1·484 (4)	O (20) 2·127 (4)	O (32) 1·875 (4)
O (6) 1·476 (4)	O (14) 1·459 (4)	O (21) 2·143 (4)	O (33) 1·869 (4)
O (7) 1·485 (4)	O (15) 1·470 (4)	Al (1)- O (22) 1·869 (4)	Average Mn-O 2·152 Å
O (8) 1·474 (4)	O (16) 1·472 (4)	O (23) 1·899 (4)	Al-O 1·884
Average S-O 1·476 Å		O (24) 1·882 (4)	
		O (25) 1·884 (4)	
		O (26) 1·885 (4)	
		O (27) 1·879 (4)	

distance was observed (this oxygen is the only one linked also to Mn) unlike what was observed in some iron sulphates, e.g. in roemerite (Fanfani, Nunzi, and Zanazzi, 1970) and in coquimbite (Giacovazzo, Menchetti, and Scordari, 1970).

The electrostatic valence balance, computed according to Brown and Shannon (1973), is on the whole satisfactory, with some exceptions, e.g. O(1) and O(30), as already discussed in the hydrogen bonding description.

TABLE VII. Bond angles and edges of polyhedra

O(1)-S(1)-O(2)	109.5(2)°	O(1)-O(2)	2.417(5) Å	O(9)-S(3)-O(10)	110.4(2)°	O(9)-O(10)	2.417(6) Å	
O(3)	109.2(2)	O(3)	2.403(6)	O(11)	108.9(2)	O(11)	2.412(5)	
O(4)	109.5(2)	O(4)	2.416(5)	O(12)	110.1(2)	O(12)	2.417(5)	
O(2)-S(1)-O(3)	110.0(2)	O(2)-O(3)	2.415(5)	O(10)-S(3)-O(11)	108.1(2)	O(10)-O(11)	2.407(5)	
O(4)	108.3(2)	O(4)	2.398(5)	O(12)	109.7(2)	O(12)	2.419(5)	
O(3)-S(1)-O(4)	110.3(2)	O(3)-O(4)	2.419(5)	O(11)-S(3)-O(12)	109.7(2)	O(11)-O(12)	2.435(5)	
O(5)-S(2)-O(6)	109.6(2)	O(5)-O(6)	2.406(5)	O(13)-S(4)-O(14)	108.4(2)	O(13)-O(14)	2.387(6)	
O(7)	108.5(2)	O(7)	2.395(5)	O(15)	109.3(2)	O(15)	2.409(5)	
O(8)	109.5(2)	O(8)	2.402(6)	O(16)	107.3(2)	O(16)	2.380(6)	
O(6)-S(2)-O(7)	108.4(2)	O(6)-O(7)	2.401(5)	O(14)-S(4)-O(15)	110.5(2)	O(14)-O(15)	2.407(6)	
O(8)	111.1(2)	O(8)	2.432(5)	O(16)	110.8(2)	O(16)	2.412(6)	
O(7)-S(2)-O(8)	109.7(2)	O(7)-O(8)	2.420(5)	O(15)-S(4)-O(16)	110.5(2)	O(15)-O(16)	2.417(5)	
Average O-O							2.410 Å	
O(16)-Mn-O(17)	85.7(1)°	O(16)-O(17)	2.905(6) Å	O(22)-Al(1)-O(23)	89.8(2)°	O(22)-O(23)	2.658(5) Å	
O(18)	88.5(2)	O(18)	3.004(5)	O(24)	90.8(2)	O(24)	2.672(5)	
O(19)	177.4(2)	O(20)	3.115(5)	O(25)	178.5(3)	O(26)	2.687(5)	
O(20)	95.2(1)	O(21)	3.033(6)	O(26)	91.5(2)	O(27)	2.617(5)	
O(21)	91.5(2)	O(17)-O(18)	2.945(6)	O(27)	88.6(2)	O(23)-O(24)	2.683(5)	
O(17)-Mn-O(18)	84.4(1)	O(19)	3.116(5)	O(23)-Al(1)-O(24)	90.4(2)	O(25)	2.644(5)	
O(19)	91.7(1)	O(21)	3.246(5)	O(25)	88.7(2)	O(27)	2.686(5)	
O(20)	172.9(2)	O(18)-O(19)	3.135(6)	O(26)	178.7(3)	O(24)-O(25)	2.644(5)	
O(21)	97.4(2)	O(20)	3.028(5)	O(27)	90.6(2)	O(26)	2.645(6)	
O(18)-Mn-O(19)	91.6(1)	O(19)-O(20)	2.965(6)	O(24)-Al(1)-O(25)	89.2(2)	O(25)-O(26)	2.666(5)	
O(20)	88.6(1)	O(21)	3.007(6)	O(26)	89.2(2)	O(27)	2.692(5)	
O(21)	178.2(3)	O(20)-O(21)	3.010(6)	O(27)	178.8(3)	O(26)-O(27)	2.656(5)	
O(19)-Mn-O(20)	87.4(1)	Average O-O		3.042 Å	O(25)-Al(1)-O(26)	90.1(2)		
O(21)	88.5(2)			O(27)	91.4(2)			
O(20)-Mn-O(21)	89.7(2)			O(26)-Al(1)-O(27)	89.8(2)			
O(28)-Al(2)-O(29)	89.5(2)°	O(28)-O(29)	2.664(5) Å	O(30)-Al(2)-O(31)	89.1(2)°	O(31)-O(32)	2.685(5) Å	
O(30)	90.8(2)	O(30)	2.699(5)	O(32)	89.4(2)	O(33)	2.692(5)	
O(31)	179.6(3)	O(32)	2.648(5)	O(33)	179.3(3)	O(32)-O(33)	2.660(5)	
O(32)	89.1(2)	O(33)	2.628(5)	O(31)-Al(2)-O(32)	91.2(2)	Average O-O		2.664 Å
O(33)	88.5(2)	O(29)-O(30)	2.652(5)	O(33)	91.7(2)			
O(29)-Al(2)-O(30)	89.1(2)	O(31)	2.671(5)	O(32)-Al(2)-O(33)	90.6(2)			
O(31)	90.2(2)	O(33)	2.676(5)					
O(32)	178.0(2)	O(30)-O(31)	2.649(5)					
O(33)	90.9(2)	O(32)	2.652(5)					

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[Manuscript received 13 May 1975]