satisfactorily bonded except for O(3), which has a net charge of $-\frac{1}{2}$. It seems probable, therefore, that the hydrogen atoms are statistically distributed over the O(3) atoms. This would also account for the very low temperature factor obtained for O(3). If the occupancy for O(3) is increased to 1·06 (to take the $\frac{1}{2}$ proton into account) and the structure refined, R decreases marginally and the temperature factor increases up to a similar value to that obtained for O(2). Clearly, this supports the statistical distribution of protons over the O(3) atoms.

Fig. 2 compares this new structure with that of the well known β-alumina ($Na_2O.11Al_2O_3$) structure (Beevers & Ross, 1937). The major difference lies within the close-packed part of the structure. In β-alumina, four close-packed layers form the so-called spinel block; this new structure has only two such layers.

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Structure of Ca-Rich Agardite, $(Ca_{0.40}Y_{0.31}Fe_{0.09}Ce_{0.06}La_{0.04}Nd_{0.01})Cu_{6.19}[(AsO_4)_{2.42}(HAsO_4)_{0.49}](OH)_{6.38}.3H_2O$

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Abstract. $M_r = 1023{\cdot}8$, hexagonal, $P6_3/m$, $a = 13{\cdot}583\,(2)$, $c = 5{\cdot}895\,(1)$ Å, $V = 941{\cdot}9\,(2)$ Å^3, $Z = 2$, $D_x = 3{\cdot}61$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 14·0 mm^{-1}, $F(000) = 484{\cdot}9$, room temperature, final $R = 0{\cdot}077$, $R_w = 0{\cdot}056$ for 1087 reflections. The specimen is from Setoda, Hiroshima, Japan. The structure consists of infinite CuO_4 chains running along the c axis, which are alternately connected to MO_9 polyhedra (M = Ca, Y, *etc.*) and AsO_4 tetrahedra. In the mixite group, the charge compensation on the substitution of a divalent cation (*e.g.* Ca^{2+}) for a trivalent cation (*e.g.* Y^{3+}) is accomplished by the concomitant substitution of OH^- for O^{2-}.

Introduction. There exist copper minerals having the general formula $MCu_6(XO_4)_3(OH)_6.3H_2O$ where M = Bi, Y, rare-earth element, Ca, Al; X = As, P, known as the mixite-group minerals. So far four minerals are known to belong to this group: agardite (M = Y, Ca; X = As; Dietrich, Orliac & Permingeat, 1969), goudeyite (M = Al, Y; X = As; Wise, 1978), mixite (M = Bi; X = As; Walenta, 1960), and petersite (M = Y, rare-earth element, Ca; X = P; Peacor & Dunn, 1982). All these minerals crystallize in the hexagonal space group $P6_3/m$ or $P6_3$ with similar lattice constants of a = 13·29–13·88 and c = 5·87–5·96 Å. Therefore, they are presumed to be isostructural. None of their crystal structures, however, has yet been reported probably because only small crystals have been found. In these minerals, isomorphous substitution of a trivalent cation by a divalent cation (*e.g.* Ca^{2+}) is frequently observed in the M site. The mechanism of the charge compensation has, for many years, posed a problem in the understanding of this mineral group. This work has been performed to elucidate the crystal structure and the substitution mechanism of mixite-group minerals.

The specimens used in the study are Ca-rich agardite from Setoda, Hiroshima prefecture, Japan. They were collected by Dr K. Masutomi and members of the Kyoto Kobutsu Kenkyukai.

Experimental. Electron microprobe analyses gave Cu, 48·97; As, 32·22; Y, 3·42; Ca, 2·57; Ce, 1·01; Fe, 0·73; La, 0·70; Nd, 0·13 wt%; Gd, trace. The corresponding unit-cell composition, normalized to 21

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oxygens and including three estimated zeolitic water molecules, is: $(Ca_{0.40}Y_{0.31}Fe_{0.09}Ce_{0.06}La_{0.04}Nd_{0.01})$-$Cu_{6.19}[(AsO_4)_{2.42}(HAsO_4)_{0.49}](OH)_{6.38}.3H_2O$ and ideally $MCu_6(AsO_4)_3(OH)_6.3H_2O$ with M = Ca, Y, *etc.*

Pale green single crystal with prismatic hexagonal shape (0·040 mm ∅ × 0·088 mm). Preliminary examination by precession camera, diffraction intensites collected on a Rigaku AFC-5 automatic four-circle diffractometer equipped with Rotaflex RU-200 X-ray generator (operating condition: 50 kV, 160 mA), using graphite-monochromated Mo $K\alpha$ radiation. Cell dimensions refined by least-squares fitting of 21 reflections with $21° < 2\theta < 33°$, intensity data collected by 2θ–ω scans, scan speed 2° min^{-1}. 3129 unique reflections up to $\sin\theta/\lambda = 1{\cdot}04$ Å^{-1}, $0 \le h \le 23$, $0 \le k \le 24$, $0 \le l \le 12$; standard reflections (400, 040, and 004) every 100 observations, 1·9% max. fluctuation. Corrections for Lorentz–polarization. Absorption correction using program *ACACA* (Wuensch & Prewitt, 1965) with 1280 sampling points and optically measured crystal dimensions, min. and max. transmission factors: 0·365 and 0·627; linear absorption coefficients from *International Tables for X-ray Crystallography* (1974). Centrosymmetric space group $P6_3/m$ indicated by Wilson's statistics using *RSWS*-3 in *UNICS* (Sakurai, 1967). Structure solved by Patterson and Fourier methods (*GSFFR*; Ohmasa, 1972). Atomic parameters refined (on F) by full-matrix least-squares method based on 1087 observed reflections $[|F_o| > 3\sigma(|F_o|)]$ with *RFINE*2 (Finger, 1969). The M site was occupied by various kinds of atoms and the scattering factor for the Y atom was used as that of the M site for simplicity. Scattering factors of neutral atoms from Cromer & Mann (1968), anomalous-dispersion factors from *International Tables for X-ray Crystallography* (1974).

Least-squares refinements with anisotropic temperature factors except for O(6) yielded $R = 0{\cdot}080$. At this stage, a difference Fourier synthesis revealed weak residues around the c axis. They were assumed to correspond to the O atom of the zeolitic water, and this atom was included in the refinement with 50% occupancy and isotropic temperature factors. Further refinement led to $R = 0{\cdot}077$, $R_w = 0{\cdot}056$, $w = 1/\sigma^2(F_o)$, with shift/error for all the parameters less than 0·01; final $\Delta\rho$ map showed maximum of 3 e Å^{-3} around the c axis and minimum of −6 e Å^{-3} at the metal atoms.

Discussion. The final atomic positional and thermal parameters are given in Table 1,* the interatomic distances and bond angles calculated with *UMBADTEA* (Finger, 1968) are listed in Table 2. Fig. 1 is a view of the structure down the c axis.

The square-planar CuO_4 groups share a pair of opposite edges to form chains along the c axis. The MO_9 polyhedra and the AsO_4 tetrahedra alternately stack parallel to the c axis and join the CuO_4 chains.

The Cu atoms are in octahedral coordination, with five O atoms in the square-pyramidal position, while the sixth octahedral position, O(6), is statistically occupied by the zeolitic water around the c axis. The presence of the zeolitic water in agardite was reported by Dietrich *et al.* (1969) after their thermal analysis. The large temperature factor of O(6) (see Table 1) may support

Table 1. *Atomic coordinates, thermal parameters* (Å^2) *with e.s.d.'s in parentheses, and the bond-valence sums* $\sum c_v$

$$B_{eq} = 4(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 - \beta_{12}ab)/3.$$

	x	y	z	B_{eq}	$\sum c_v$
Cu	0·41184 (9)	0·31497 (9)	−0·0021 (2)	0·89	----
Y	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{1}{4}$	0·79	----
As	0·3438 (1)	0·4948 (8)	$\frac{1}{4}$	0·65	----
O(1)	0·1989 (7)	0·4125 (8)	$\frac{1}{4}$	0·84	2·03
O(2)	0·3920 (8)	0·4011 (8)	$\frac{1}{4}$	0·92	2·08
O(3)	0·5725 (5)	0·1808 (5)	−0·016 (1)	1·13	1·78
O(4)	0·4400 (9)	0·2444 (8)	$\frac{1}{4}$	1·39	1·23
O(5)	0·3766 (8)	0·0090 (8)	$\frac{1}{4}$	0·90	1·01
O(6)	0·156 (4)	0·007 (4)	−0·065 (7)	15 (1)*	0

* Isotropic temperature factor.

Table 2. *Selected bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s*

Cu–O(1)	2·011 (8)	O(1)–Cu–O(3)	91·6 (3)
Cu–O(2)	1·991 (9)	O(1)–Cu–O(4)	98·7 (4)
Cu–O(3)	2·321 (8)	O(1)–Cu–O(5)	81·7 (3)
Cu–O(4)	1·908 (9)	O(1)–Cu–O(6)	90·8 (8)
Cu–O(5)	1·924 (6)	O(2)–Cu–O(3)	95·1 (3)
Cu–O(6)	3·14 (7)	O(2)–Cu–O(4)	80·4 (4)
		O(2)–Cu–O(5)	98·5 (4)
M–O(3)	2·395 (6) (×6)	O(3^i)–M–O(3^{ii})	81·8 (2)
M–O(4)	2·687 (11) (×3)	O(3^i)–M–O(3^{iii})	81·8 (3)
		O(3)–M–O(4)	68·2 (3)
As–O(1)	1·710 (8)	O(1)–As–O(2)	105·0 (5)
As–O(2)	1·689 (13)	O(1)–As–O(3)	111·9 (3)
As–O(3)	1·659 (6) (×2)	O(2)–As–O(3)	107·5 (3)

Symmetry code: (i) x, y, z; (ii) $y - x, -x, z$; (iii) $x, y, -z$.

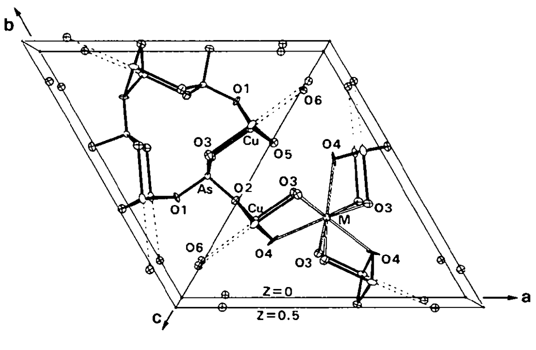

Fig. 1. An *ORTEP* (Johnson, 1976) view of Ca-rich agardite down the c axis with 50% probability thermal ellipsoids.

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* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39796 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the zeolitic nature of the water molecules. The Jahn–Teller effect is observed in the Cu octahedron. The As atom exhibits the usual tetrahedral coordination by O atoms. The *M* atom shows (6 + 3) coordination by the O atoms in the form of a tricapped trigonal prism. The trigonal planes are perpendicular to the *c* axis.

The H atoms could not be located in the difference Fourier maps. To distinguish O^{2-}, OH^-, and H_2O in the oxygen positions, the bond-valence sums were calculated following the method of Donnay & Allmann (1970) using the values of the bond lengths and coordination numbers. This method is based on Pauling's (1929) principle of local neutralization of charge. The ideal values of the bond-valence sums are 2, 1, and 0 for O^{2-}, OH^-, and H_2O, respectively. The bond-valence sums $\sum c_v$, listed in Table 1, clearly show that O(1) and O(2) are oxygen ions, while O(4) and O(5) correspond to the hydroxyl group. In contrast the valence sum of atom O(3) is 1·78, suggesting the presence of partial substitution of oxygen ions by the hydroxyl ion in this position. Accordingly, it is found that, on substitution of Ca^{2+} for a trivalent cation, the charge compensation is accomplished by the concomitant substitution of OH^- for O^{2-} at the O(3) position.

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Tetracaesium Divanadate Dihydrate, $Cs_4V_2O_7.2H_2O$

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Abstract. $M_r = 781\cdot53$, monoclinic, $P2_1/c$, $a = 9\cdot196\,(1)$, $b = 17\cdot863\,(2)$, $c = 9\cdot059\,(1)$ Å, $\beta = 111\cdot81\,(1)°$, $V = 1381\cdot6\,(2)$ Å^3, $Z = 4$, $D_x = 3\cdot757$ Mg m^{-3}, $\lambda(\text{Mo }K\bar{\alpha}) = 0\cdot71073$ Å, $\mu = 12\cdot0$ mm^{-1}, $F(000) = 1368$, $T = 298$ K. Final $R = 0\cdot071$ for 3417 unique observed reflections. The V_2O_7 group has a nearly staggered conformation with a V—O—V angle of 174 (1)°. The Cs^+ ions are surrounded by eight to nine O atoms of the V_2O_7 groups and the H_2O molecules.

Introduction. An unknown, highly hygroscopic phase was obtained from aqueous solution of $2Cs_2O.V_2O_5$ by evaporation at 373 K. A structure determination revealed its chemical composition to be $Cs_4V_2O_7.2H_2O$.

Experimental. Crystal of irregular rounded shape 0·15 × 0·2 × 0·3 mm, enclosed in thin-wall (0·01 mm) glass capillary. Four-circle Rigaku diffractometer, lattice constants based on 29 reflections with $29 < 2\theta < 35°$. Intensity measurement up to $(\sin\theta)/\lambda = 0\cdot704$ Å^{-1} within the range h ±12, k 0→25, l ±12 performed in several separate runs; frequent redetermination of the orientation matrix necessary. $2\theta/\omega$-scanning, scanning range $\Delta\omega = 1\cdot2° + 0\cdot5° \tan\theta$ and speed 2° min^{-1}. Absorption correction not practicable because of difficulties in measuring specimen shape. Intensities reduced to common scale using standard reflections $\bar{2}40$, $30\bar{2}$ and $\bar{4}00$. 8247 reflections measured, 1697 unobserved [$I < \sigma(I)$ or too weak to be scanned], 6550 considered observed, 3417 unique reflections, $R_{\rm int} = \sum|F_j - \bar{F}_j|/\sum F_j = 0\cdot059$. Structure

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