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Tachyhydrite, Dimagnesium Calcium Chloride 12-Hydrate

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Abstract. $[CaCl_6][Mg(H_2O)_6]_2$, rhombohedral, $R\bar{3}$, hexagonal cell $a = 10\cdot136\ (1)$, $c = 17\cdot318\ (2)$ Å, $Z = 3$, $D_x = 1\cdot673$ Mg m^{-3}, Mo $K\alpha$ radiation ($\lambda = 0\cdot71069$ Å), $\mu = 11\cdot18$ mm^{-1}. Full-matrix least-squares refinement of 1394 nonequivalent *hkl* gave $R = 0\cdot042$ and $R_w = 0\cdot051$. The structure contains isolated, octahedrally coordinated cations, with distances Ca—Cl 2·752 (2) (6×); Mg—O 2·059 (6) (3×), 2·062 (6) Å (3×). Only hydrogen bonds from H_2O to Cl, average distance 3·229 Å, hold the octahedra together. The structure is similar to that reported for $NiSnCl_6.6H_2O$ and related compounds.

Introduction. This study was initiated in connection with a program on the nature of physical and chemical interactions in salts that might be used for radioactive-waste disposal (Stewart & Potter, 1979). Tachyhydrite appeared to be of interest because of its occurrence in evaporite deposits, its high water content, and its unusually wide stability field (in equilibrium with mother liquor) over temperatures from 295 K to at least 440 K (van't Hoff & Kenrick, 1897). Data on its synthesis, crystallography, and powder pattern were reported by Erd, Clynne, Clark & Potter (1979). The synthetic crystal selected for collection of intensity data was an approximately spherical fragment, about 0·3 mm in diameter. Because of the extreme deliquescence of tachyhydrite, the crystal was sealed, together with the saline solution with which it was in equilibrium, in a glass capillary tube. A glass rod 0·2 mm thick was inserted into the capillary to hold the crystal stationary, and the capillary was sealed with a cyanoacrylate cement. About 2200 reflections were measured, as well as a standard after every 30 measurements; the standard varied in intensity only by about 3% during the data collection, so apparently no deterioration of the crystal occurred. Numerous strong reflections were remeasured, with additional filters, and scaled. X-ray absorption in the specimen was considered to be negligible and no correction was applied, but dispersion corrections were included. Equivalent *hkl*'s were averaged to obtain 1394 nonequivalent reflections, of which 1024 had $|F| > 3\sigma|F|$, where σ was based on counting statistics.* Computer programs by Stewart (1976) were used throughout the study, together with scattering factors in the analytical form for neutral atoms developed by Doyle & Turner (1968).

The structure of tachyhydrite was presumed at the start to be composed of independent octahedral units, $[CaCl_6]^{4-}$ and $[Mg(H_2O)_6]^{2+}$. An initial model, with Ca at 0,0,0, Mg at 0,0,$\frac{1}{3}$, and Cl atoms located with the aid of a Patterson map, gave a conventional $R = 0\cdot50$. Least-squares refinement with isotropic temperature factors reduced R to 0·08 in two cycles. Anisotropic refinement was continued in space group $R3$ to $R = 0\cdot046$. The result of this acentric refinement was not considered entirely satisfactory because of the appearance of unexpected distortions in the $Mg(H_2O)_6$ octahedron (Mg—O distances 2·10 and 2·01 Å) and the relatively large standard errors. A test of the normalized structure factor statistical distributions at this point strongly indicated a centrosymmetric structure; therefore, a new refinement in space group $R\bar{3}$ was carried out. This process led to $R = 0\cdot042$; the distortions observed in the earlier refinement completely disappeared, and the standard errors of the variable parameters were greatly reduced. This experiment provides another example of the dangers of attempting to refine a structure that is actually centrosymmetric in a noncentrosymmetric setting, as pointed out recently by Marsh & Schomaker (1979).

The largest maxima on the final difference Fourier map were 0·5 e Å^{-3}. Four H atoms were placed in reasonable locations and four cycles of refinement for

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* The four strongest reflections (033, 006, $\bar{1}23$, $\bar{1}32$) are not included in this total because of difficulties with scaling.

Table 1. *Comparison of structure parameters of tachyhydrite of Clark, Evans & Erd* (1) *with those of Leclaire, Borel & Monier* (2)

Standard deviations are given in parentheses in terms of the last digit. The anisotropic temperature factors are given as $U \times 100$ Å^2, corresponding to $\exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{23}klb^*c^*)]$. The data of (2) are transformed to our setting by means of the matrix: $(-\frac{1}{3},\frac{2}{3},-\frac{1}{3}/\frac{1}{3},\frac{1}{3},-\frac{2}{3}/\frac{1}{3},\frac{1}{3},\frac{1}{3})$.

Unit cell	a (Å)	c (Å)	V (Å^3)
(1)	10·136 (1)	17·318 (2)	1540·9
(2)	10·120 (2)	17·325 (3)	1536·5

Structure	Site in $R\bar{3}$	x	y	z	$\bar{u}$ (Å) (r.m.s.)	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca (1)	3(a)	0	0	0	0·179 (2)	3·10 (6)	$=U_{11}=2U_{12}$	3·38 (6)	1·55 (2)	0	0
(2)		0	0	0	0·168 (1)						
Mg (1)	6(c)	0	0	0·3243 (1)	0·177 (2)	3·02 (8)	$=U_{11}=2U_{12}$	3·34 (8)	1·51 (3)	0	0
(2)		0	0	0·32405 (4)	0·170 (1)						
Cl (1)	18(f)	0·1780 (1)	−0·0688 (1)	0·0926 (1)	0·213 (2)	4·76 (5)	4·65 (4)	4·23 (4)	2·99 (4)	−0·44 (3)	−0·36 (3)
(2)		0·17814 (5)	−0·06884 (5)	0·09254 (8)	0·198 (1)						
O(1) (1)	18(f)	0·1882 (3)	0·0700 (3)	0·2548 (1)	0·210 (3)	3·8 (1)	5·2 (1)	4·2 (1)	1·6 (1)	0·6 (1)	0·0 (1)
O(2) (2)		0·18867 (18)	0·07053 (18)	0·25502 (24)	0·211 (1)						
O(2) (1)	18(f)	−0·1897 (3)	−0·0628 (3)	0·3920 (3)	0·227 (3)	4·5 (1)	5·0 (2)	6·0 (2)	2·3 (1)	1·6 (1)	0·4 (1)
O(1) (2)		−0·19000 (18)	−0·06329 (18)	0·39142 (24)	0·211 (1)						

Table 1 (*cont.*)

	Site in $R\bar{3}$	x	y	z	$\bar{u}$ (Å)
H(1) (1)	18(f)	0·18 (1)	0·04 (1)	0·206 (6)	0·3 (2)
H(21) (2)		0·181 (4)	0·035 (4)	0·207 (6)	0·16 (2)
H(2) (1)	18(f)	0·27 (1)	0·18 (1)	0·263 (5)	0·2 (2)
H(22) (2)		0·270 (7)	0·151 (7)	0·255 (10)	0·22 (2)
H(3) (1)	18(f)	−0·20 (1)	0·02 (1)	0·416 (3)	0·1 (1)
H(11) (2)		−0·209 (8)	0·001 (8)	0·402 (12)	0·26 (2)
H(4) (1)	18(f)	−0·23 (1)	−0·16 (1)	0·417 (6)	0·3 (2)
H(12) (2)		−0·245 (8)	−0·141 (8)	0·400 (12)	0·26 (2)

H atom parameters x, y, z and U, using 270 structure factors with $(\sin\theta)/\lambda < 0·45$ Å^{-1}, reduced R for this set from 0·044 to 0·034. The final positional accuracy of the atoms is 0·002 Å for Ca, Mg and Cl, 0·003 Å for O, and 0·1 Å for H. The final structural and thermal parameters are given in Table 1. X-ray powder data for tachyhydrite published by Erd *et al.* (1979), have been found to agree reasonably well with corresponding data calculated from the structure reported here.*

Discussion. The crystal structure is illustrated in Fig. 1 where the isolated, octahedral groups are shown, as well as their packing and the O···Cl hydrogen bonds that hold the groups together. Bond distances and angles are listed in Table 2. All appear normal compared with others reported in the literature; for example, Ca is coordinated by six Cl in β-$CaCl_2.4H_2O$ (Leclaire & Borel, 1978), average Ca—Cl 2·740 Å, and Mg is octahedrally coordinated by H_2O in $MgCl_2.12H_2O$ (Sasvári & Jeffrey, 1966), average Mg—O 2·062 Å. Both these structures have O···Cl hydrogen bonds, with average distances of 3·241 Å in β-$CaCl_2.4H_2O$ and 3·194 Å in $MgCl_2.12H_2O$, compared with the present O···Cl average of 3·229 Å. Bond-strength summations are completely satisfactory with the simple ionic model: Ca—Cl, Mg—O $\frac{1}{3}$; H—O $\frac{5}{6}$; H···Cl $\frac{1}{6}$. The shortest (3·120 Å) and, therefore, strongest hydrogen bonds join each $CaCl_6$ group to one $Mg(H_2O)_6$ group above and one below through O(1); the integrity of this trimolecular unit may be related to the stability of the crystals up to the relatively high

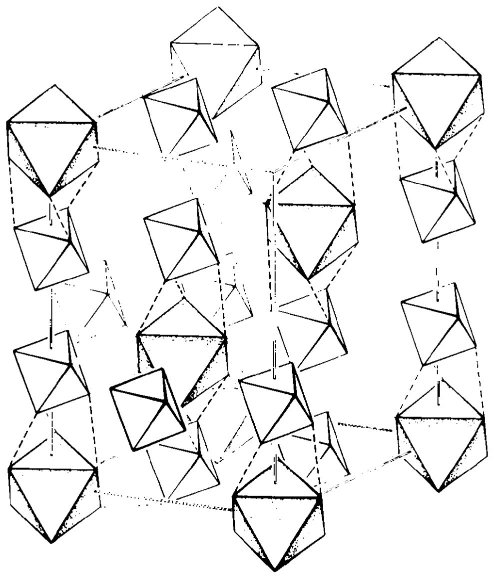

Fig. 1. Crystal structure of tachyhydrite. The c axis is vertical. Shaded octahedra are $CaCl_6$ groups; unshaded, smaller octahedra are $Mg(H_2O)_6$ groups. Dashed lines indicate hydrogen bonds; the shortest bonds are emphasized.

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* Lists of structure factors, thermal ellipsoids and observed/calculated powder data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35325 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and angles* (°) *in tachyhydrite*

Standard deviations are given in parentheses in terms of the last digit. Subscripts 01...06 (or no subscript) indicate atoms in basic set (*International Tables for X-ray Crystallography*, 1952), 11...16 basic set $+\frac{2}{3},\frac{1}{3},\frac{1}{3}$, 21...26 basic set $+\frac{1}{3},\frac{2}{3},\frac{2}{3}$ (sometimes in adjacent cell).

The $CaCl_6$ octahedron			
Ca–Cl (6×)	2·752 (2)	Cl_{01}–Ca–Cl_{02} (6×)	89·48 (5)
		–Cl_{05} (6×)	90·52 (6)
Cl_{01}–Cl_{02} (6×)	3·874 (3)	–Cl_{04} (3×)	180
–Cl_{05} (6×)	3·908 (2)		
The $Mg(H_2O)_6$ octahedron			
Mg–O(1) (3×)	2·059 (6)	$O(1)_{01}$–Mg–$O(1)_{02}$ (3×)	89·2 (3)
Mg–O(2) (3×)	2·062 (6)	–$O(2)_{02}$ (3×)	91·4 (3)
		–$O(2)_{03}$ (3×)	88·4 (3)
$O(1)_{01}$–$O(1)_{02}$ (3×)	2·894 (9)	$O(2)_{01}$–Mg–$O(2)_{02}$ (3×)	91·0 (3)
–$O(2)_{02}$ (3×)	2·949 (6)	$O(1)_{01}$–Mg–$O(2)_{01}$ (3×)	177·5 (3)
–$O(2)_{03}$ (3×)	2·873 (7)		
$O(2)_{02}$–$O(2)_{02}$ (3×)	2·938 (9)		
Hydrogen bonds			
$O(1)_{01}$–Cl_{01}	3·120 (4)	Cl_{01}–$O(1)_{01}$–Cl_{14}	101·8 (1)
–Cl_{14}	3·226 (3)	H(1)–$O(1)_{01}$–H(2)	114 (8)
–H(1)	0·9 (1)	$O(1)_{01}$–H(1)–Cl_{01}	172 (4)
–H(2)	1·0 (1)	$O(1)_{01}$–H(2)–Cl_{14}	158 (5)
H(1)···Cl_{01}	2·22 (8)		
H(2)···Cl_{14}	2·25 (9)		
$O(2)_{01}$–Cl_{11}	3·215 (5)	Cl_{11}–$O(2)_{01}$–Cl_{12}	158·5 (1)
–Cl_{12}	3·356 (6)	H(3)–$O(2)_{01}$–H(4)	121 (7)
–H(3)	1·0 (1)	$O(2)_{01}$–H(3)–Cl_{11}	154 (3)
–H(4)	1·0 (1)	$O(2)_{01}$–H(4)–Cl_{12}	153 (5)
H(3)···Cl_{11}	2·31 (7)		
H(4)···Cl_{12}	2·44 (9)		
Other close approaches			
$O(1)_{01}$–Cl_{13}	3·607 (4)		
$O(2)_{01}$–$O(2)_{24}$	3·299 (5)		
$O(1)_{01}$–$O(2)_{25}$	3·319 (10)		

Comparison with the results of Leclaire, Borel & Monier (2)

Ca–Cl	(1)	2·752 (2)	O(1)–H(1)	(1)	0·9 (1)
	(2)	2·7497 (7)	O(2)–H(21)	(2)	0·89 (3)
Mg–O(1)	(1)	2·059 (6)	O(1)–H(2)	(1)	1·0 (1)
Mg–O(2)	(2)	2·055 (1)	O(2)–H(22)	(2)	0·82 (3)
Mg–O(2)	(1)	2·062 (6)	O(2)–H(3)	(1)	1·0 (1)
Mg–O(1)	(2)	2·059 (1)	O(1)–H(12)	(2)	0·80 (4)
			O(2)–H(4)	(1)	1·0 (1)
			O(1)–H(11)	(2)	0·71 (4)

temperature reported (~443 K). O(1) also is tied to an adjacent Cl atom by a longer hydrogen bond nearly parallel to the *xy* plane. O(2) has two similar bonds, so each Cl atom receives four hydrogen bonds. The trimolecular groups are cross-linked only by these weak hydrogen bonds. As the structure consists simply of one trimolecular group at each lattice point, cleavage would be expected along the plane with the largest spacing, namely $\{10\bar{1}1\}$; this cleavage is, in fact, observed to be perfect (Palache, Berman & Frondel, 1951).

A view of the octahedral groups showing thermal ellipsoids is given in Fig. 2. The cation and Cl ellipsoids are very nearly spherical, the average r.m.s. displacement being 0·19 Å. As might be expected, the thermal motion is greater for the water molecules and their ellipsoids are more elongated, particularly for O(2) which has maximum r.m.s. displacement 0·26 Å; this water molecule forms the weakest hydrogen bonds.

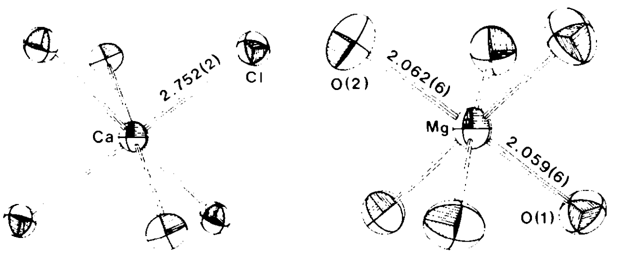

Fig. 2. *ORTEP* (Johnson, 1965) drawing showing thermal ellipsoids at the 50% probability level for the cation octahedra in tachyhydrite, with *b* horizontal, *c* vertical. (Distances are in Å.)

The syntheses of two related dodecahydrates were reported by Ferrari & Cavalca (1946), who gave the formulae as $MnCl_2.2MgCl_2.12H_2O$ and $CdCl_2.2NiCl_2.12H_2O$. Almost certainly these are structurally $[Mg(H_2O)_6]_2[MnCl_6]$ and $[Ni(H_2O)_6]_2[CdCl_6]$, by analogy to tachyhydrite. From Laue and rotation patterns, Ferrari & Cavalca (1946) derived unit cells in the trigonal space group $P\bar{3}$ (or $P3$) with $a = 9{\cdot}46$ and $c = 11{\cdot}11$ Å for the former and $a = 9{\cdot}76$ and $c = 11{\cdot}35$ Å for the latter, each containing two formula units. Thus, the structures of these compounds are different from that of tachyhydrite, but their crystal-chemical principles must be similar. The compound $NiSnCl_6.6H_2O$, with structural formula $[Ni(H_2O)_6][SnCl_6]$ as reported by Pauling (1930), has a structure in space group $R\bar{3}$ very similar to that of tachyhydrite, but has a c axis approximately $\frac{2}{3}$ as large, because there are only two molecular groups in the formula unit instead of three. Pauling pointed out that 'Groth lists 35 similarly crystallizing hexahydrated double halides of bivalent and quadrivalent elements... and further members of the series have since been discovered'. We have found reference to only one other structural study for this large group of compounds, that of $[Mg(H_2O)_6][TeX_6]$ where X = Cl, Br, I by Angoso, Onken & Hahn (1964) [for X = Cl, $R(hk0) = 0{\cdot}25$]. Thus, it appears that further syntheses and structural work could yield valuable information about ionic radii, atomic substitutions, thermal motions, and water–halogen hydrogen bonding in all these hydrated halides.

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Note added in proof: Only late in the editorial process was it discovered that a structure for this same crystal had also been determined by Leclaire, Borel & Monier (1980) (preceding paper) and reported under the alternative name tachydrite. The structure of Leclaire *et al.* (refined to $R = 0\cdot021$) is in close agreement with ours. As shown in Table 1, the differences between the structure parameters are not greater than the sum of the reported standard errors, except for $z_{\rm Mg}$ and $y_{\rm H(2)}$ where they are $1\cdot7(\sum\sigma)$. The standard errors given by Leclaire *et al.*, are generally less than ours, and the hydrogen atoms are somewhat better resolved. We believe, however, that in the case of the unit-cell parameters, where the differences are more substantial, the results of Erd *et al.* (1979), obtained from a calibrated powder diffractometer pattern made with Cu $K\alpha$ radiation, are more reliable.

References

ANGOSO, A., ONKEN, H. & HAHN, H. (1964). *Z. Anorg. Chem.* **328**, 223–230.

ERD, R. C., CLYNNE, M. A., CLARK, J. R. & POTTER, R. W. II (1979). *J. Appl. Cryst.* **12**, 481–482.

DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* A**24**, 390–397.

FERRARI, A. & CAVALCA, L. (1946). *Rend. Soc. Mineral. Ital.* **3**, 117–120.

HOFF, J. H. VAN'T & KENRICK, F. B. (1897). *Sitzungsber. Preuss. Akad. Wiss. Phys. Math. Kl.* pp. 508–515.

International Tables for X-ray Crystallography (1952). Vol. I. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.

LECLAIRE, A. & BOREL, M. (1978). *Acta Cryst.* B**34**, 900–902.

LECLAIRE, A., BOREL, M. M. & MONIER, J. C. (1980). *Acta Cryst.* B**36**, 2734–2735.

MARSH, R. E. & SCHOMAKER, V. (1979). *Inorg. Chem.* **18**, 2331–2336.

PALACHE, C., BERMAN, H. & FRONDEL, C. (1951). *Dana's System of Mineralogy*, 7th ed., Vol. II, p. 95. New York: John Wiley.

PAULING, L. (1930). *Z. Kristallogr.* **72**, 482–492.

SASVÁRI, K. & JEFFREY, G. A. (1966). *Acta Cryst.* **20**, 875–881.

STEWART, D. B. & POTTER, R. W. II (1979). *Scientific Basis for Nuclear-Waste Management*, Vol. I, edited by G. J. MCCARTHY, pp. 297–311. New York: Plenum.

STEWART, J. M. (1976). The XRAY 76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

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Manganese(II) Sulfite Trihydrate

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Abstract. α-MnSO$_3$.3H$_2$O, monoclinic, $P2_1/n$, $a = 6\cdot659\,(2)$, $b = 8\cdot920\,(2)$, $c = 8\cdot806\,(2)$ Å, $\beta = 96\cdot10\,(2)°$, $Z = 4$, $D_x = 2\cdot41$ Mg m^{-3}, μ(Mo $K\alpha$) = $2\cdot99$ mm^{-1}. Final $R = 0\cdot049$ for 1449 diffractometer data. The structure is isomorphous with α-FeSO$_3$.3H$_2$O [L.-G. Johansson & O. Lindqvist (1979). *Acta Cryst.* B**35**, 1017–1020].

Introduction. Georgii & Barrie (1976) have shown that Mn^{2+} and Fe^{2+} have high catalytic activity in the oxidation reaction $SO_2 + \frac{1}{2}O_2 + H_2O \rightarrow H_2SO_4$. In order to investigate the relations between the dimensions and the stability of the sulfite ion the structure of α-MnSO$_3$.3H$_2$O has been refined. Crystals of α-MnSO$_3$.3H$_2$O were prepared in the same way as for the isomorphous α-FeSO$_3$.3H$_2$O (Bugli & Pannetier, 1968). They have a pale rose colour and oxidize slowly in air like α-FeSO$_3$.3H$_2$O.

A crystal $0\cdot1 \times 0\cdot2 \times 0\cdot2$ mm was mounted in a glass capillary on a Syntex $P2_1$ diffractometer. Graphite-monochromated Mo $K\alpha$ radiation and a variable scan rate and range were used. 1738 reflections with $h \geq 0$ and $k \geq 0$ were measured out to $2\theta = 60°$, and 1449 were considered significant having

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