Acta Cryst. (1972) **B28**, 3572

Survey of the Geometry and Environment of Water Molecules in Crystalline Hydrates Studied by Neutron Diffraction*

By Giovanni Ferraris and Marinella Franchini-Angela

Istituto di Mineralogia e Geochimica dell' Università, Via San Massimo 24, 10123 *Torino, Italy*

(*Received* 12 *June* 1972)

The bond lengths and angles in water molecules, derived from over 40 neutron-diffraction studies of crystalline hydrates, are analysed statistically. A 'quasi-normal' spread of the dimensions and consequent deviations from an average model, affecting both water molecules and their environment, is associated with strains due to local failures of Pauling's second rule. This interpretation is consistent with linear correlations between pairs of bond lengths and/or angles. A new, more general classification of water molecules in crystalline hydrates, based on cation coordination, is proposed. The water molecules are arranged in five classes, according to the number of coordinated cations and to the position of the cations with respect to the lone-pair orbitals; each class may be further subdivided on the basis of the chemical nature of the cations.

Introduction

The water molecule plays an important role in the packing of crystalline hydrates, both because it participates in hydrogen bonds linking anions and also because, through its lone-pair orbitals, it is a satisfactory ligand for many cations.

The approximately tetrahedral environment usually assumed by the water molecule has often been idealized and used for tentative estimates of the hydrogen-atom coordinates; constant molecular geometry and, sometimes, linearity of hydrogen bonds and/or planarity of the water-acceptor group are assumed. In fact, both the conformation of the water molecule and the geometry of its environment do depend, to some extent, on the specific situations in different compounds.

Neutron diffraction is the only technique that allows unambiguous location of hydrogen atoms of the water molecule in solid hydrates with estimated standard deviations (e.s.d.'s) comparable with those of the other atoms; while very accurate X-ray data may allow the location of hydrogen atoms, their e.s.d.'s are generally too high for quantitative discussion.

Of the fifty or so crystal structures of hydrates (April 1972) studied in three dimensions by neutron diffraction, the results for 41 are reviewed here, with the 90 water molecules involved. Compounds with disorder in water molecules (*cf.* Ferraris, Jones & Yerkess, 1972*b*) or other atoms or atomic groups (*cf.* some alums) have been excluded.

The appropriate planes (Fig. 1) and bond lengths and angles were recomputed and are summarized in Tables 1 and 2 according to a classification reported below. All distances and angles are uncorrected for thermal motion since, even when reported, such corrections are merely indicative. While Tables 1 and 2 deal with all types of hydrogen bonds involving water molecules, the results to be discussed concern mainly O···O hydrogen bonds, since only for these does the number of cases studied by neutron diffraction allow statistical correlations.

The following symbols are used (Fig. 1):

W = oxygen atom of the water molecule;
H1, H2 = hydrogen atoms of the water molecule;
$A1, A2$ = acceptors of hydrogen bonds;
$C1, C2, C3$ = atoms contacting W;
φ = H–W–H angle;
$\varphi_1 = A1\cdots W\cdots A2$ angle;
$\alpha_1, \alpha_2 = W$–H$\cdots A$ angles;
δ_1, δ_2 = angles between $W\cdots C1$ and W–H;
π = plane of the water molecule;
π_1 = plane of W, $C2$ and $C3$;
γ_1, γ_2 = angles between H$\cdots A$ and π;
$\varepsilon_1, \varepsilon_2, \varepsilon_3$ = angles between $W\cdots C$ and π;
$\varepsilon = C2\cdots W\cdots C3$ angle;
ψ = angle between π and π_1;
ω_1, ω_2 = angles between the π–π_1 intersection straight line and W–H.

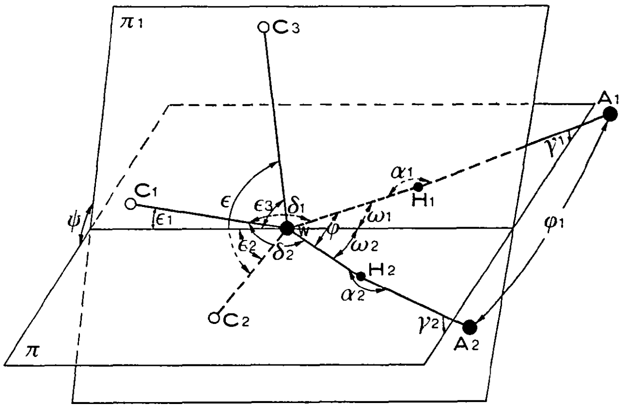


Fig. 1. Sketch of a water molecule with its environment.

---

* Paper presented at the 6th Hungarian Conference on X-ray, Electron, and Neutron Diffraction; 28th May–1st June 1972, Siófok, Hungary. Research supported by the C.N.R.

Table 1. *Distances* (Å) *and angles* (°) (*e.s.d.'s below*) *characterizing the water molecule and its environment in crystalline hydrates. Case of only one atom coordinated by W.*

The meaning of the symbols is shown in Fig. 1

Class 1, Type *D*

	W-H1	*W*-H2	*W*···*A*1	*W*-*A*2	H1···*A*1	H2···*A*2	*W*···*C*1	φ	φ_1	α_1	α_2	γ_1	γ_2	δ_1	δ_2	ε_1
$Ba(ClO_3)_2.H_2O$	0·927	0·927	2·892	2·892	1·991	1·991	2·732	110·6	128·8	163·6	163·6	−9·9	9·9	124·7	124·7	0
Sikka *et al.* (1968)	9	9	3	3	9	9	Ba 8	8	1	8	8			5	5	
$BeSO_4.4H_2O$	0·968	0·971	2·618	2·685	1·657	1·719	1·619	112·8	114·6	171·7	172·3	−0·2	−5·8	118·1	126·1	16·1
Sikka & Chidambaram (1969)	9	6	6	6	9	6	Be 5	8	2	8	7			6	6	
$CaHAsO_4.2H_2O$	0·96	0·92	2·787	3·074	1·85	2·18	2·395	105	91·1	166	167	2·2	11·4	136	119	5·0
Ferraris *et al.* (1971*a*)	3	4	12	*W* 16	3	3	Ca 10	3	4	3	3			2	2	
$CaHAsO_4.H_2O$	0·953	0·944	2·799	2·815	1·905	1·978	2·364	113	147·7	155	147	7·4	−17·7	124·9	120·7	−10·1
Ferraris *et al.* (1972*a*)	11	10	6	6	11	11	Ca 7	1	2	1	1			7	8	
$CaHPO_4.2H_2O$	0·944	0·947	2·831	3·086	1·902	2·160	2·383	105	89·8	167	166	2·6	9·8	138	116	10·2
Curry & Jones (1971)	10	17	6	*W* 11	10	17	Ca 5	1	3	2	2			1	1	
$CaSO_4$ $2H_2O$	1·002	0·981	2·817	2·824	1·815	1·844	2·338	106	105·7	178	178	0·8	1·3	117	137	7·9
Atoji & Rundle (1958)	24	25	11	11	24	24	Ca 9	2	6	1	1			2	4	
$Cd(NO_3)_2.4D_2O$	0·980	0·936	2·968	2·873	1·991	1·952	2·248	103	106·9	175	168	−4·5	12·0	121	128	22·9
McDonald & Sikka (1969)	D 17	D 20	15	*W* 20	17	19	Cd 16	2	6	2	2			1	1	
$CuCl_2$ $2H_2O$	0·946	0·946	3·176	3·176	2·239	2·239	1·922	110·0	97·3	170·7	170·7	−2·2	2·2	125·0	125·0	0
Peterson & Levy (1957)			Cl	Cl			Cu									
$CuF_2.2H_2O$ (4·2°K)	0·959	0·959	2·653	2·653	1·708	1·708	1·945	110·4	96·4	167·8	167·8	−5·2	5·2	124·8	124·8	0
Abrahams (1962)	6	6	F 1	F 1	6	6	Cu 4	4	1	6	6			3	3	
CuF_2 $2H_2O$ (298°K)	0·981	0·981	2·647	2·647	1·688	1·688	1·941	115·2	96·8	164·9	164·9	−3·7	3·7	122·4	122·4	0
Abrahams & Prince (1962)	7	7	F 1	F 1	7	7	Cu 5	5	1	8	8			4	4	
$CuSO_4.5H_2O$	0·97	0·97	2·75	2·70	1·79	1·73	1·980	114	119	168	176	11·3	1·4	125·9	119·3	−6·1
Bacon & Curry (1962)							Cu									
	0·96	0·94	2·68	2·72	1·72	1·79	1·944	109	105	173	167	2·6	5·5	126·1	125·2	0·0
							Cu									
$K_2CuCl_4.2H_2O$	0·956	0·956	3·116	3·116	2·165	2·165	1·972	109·7	100·3	173·3	173·3	0·0	0·0	125·2	125·2	0·1
Chidambaram *et al.* (1970)	6	6	Cl 1	Cl 1	6	6	Cu 4	3	1	5	5			3	3	
$MgSO_4.7H_2O$	0·976	0·963	2·703	2·768	1·732	1·810	2·056	109·9	117·2	172·8	172·9	0·8	5·6	118·7	122·6	27·4
Ferraris *et al.* (1972*d*)	9	9	6	6	9	9	Mg 5	8	2	8	8			8	8	
	0·975	0·967	2·825	2·692	1·854	1·726	2·050	109·1	105·3	173·9	176·4	1·2	−3·5	127·0	121·7	−13·4
	9	9	6	6	9	9	Mg 5	8	2	8	8			8	8	
	0·956	0·950	2·704	2·982	1·758	2·089	2·051	105·4	101·0	169·7	156·0	−8·9	−22·6	124·8	125·7	−17·7
	9	9	6	6	9	9	Mg 5	8	2	8	8			8	8	
	0·952	0·957	2·902	2·792	1·961	1·842	2·070	110·6	117·9	169·6	172·0	−9·8	1·4	123·3	126·0	3·5
	9	9	*W* 6	*W* 6	9	9	Mg 5	8	2	8	8			8	8	
$MgSO_4.4H_2O$	0·970	0·952	2·885	2·754	1·920	1·818	2·053	110	105·2	174	167·6	4·9	12·1	123·4	120·4	22·1
Baur (1964)	11	12	6	6	11	12	Mg 5	1	2	1	9			8	7	
	0·958	0·981	2·831	2·734	1·902	1·754	2·073	109	114·3	163	178	15·3	1·4	119·0	126·0	−22·9
	12	10	5	6	11	10	Mg 5	1	2	1	1			7	7	
				3·042		2·389			146·8		127		−25·3			
				5		17			2		1					
	0·968*	0·931	2·835	3·282	1·947	2·588	2·088	111	91·8	151	132	−12·7	−3·2	116·1	124	−27·8
	15	18	5	6	16	18	Mg 5	1	2	1	1			9	1	
			2·860		2·064				137·5	140		4·8				
			5		12				2	1						
	0·952†	0·990	3·080	2·834	2·419	1·848	2·072	109	70·8	126	174	−1·7	−5·8	122·0	126·7	−14·6
	12	11	*W* 6	5	13	10	Mg 5	1	1	1	1			8	8	

Table 1 (*cont.*)

$MnCl_2.4H_2O$ El Saffar & Brown (1971)	0·955 3	0·924 4	3·202 Cl 1	3·117 Cl 1 3·417 Cl 1	2·294 3	2·496 4 2·949 4	2·188 Mn 1	112·4 3	143·2 1 74·5 1	158·7 2	148·3 3 113·0 3	−6·5	−15·8 −7·0	120·8 2	126·5 2	5·0
	0·942 3	0·954 3	3·291 Cl 1	2·964 *W* 2	2·375 3	2·014 3	2·203 Mn 2	111·4 2	109·3 1	164·4 2	174·4 2	13·0	44·4	125·4 2	122·7 2	6·3
$Mn(HCO_2)_2.2H_2O$ Kay *et al.* (1968)	0·950 30	0·879 23	2·804 17	2·706 18	1·860 29	1·829 22	2·131 Mn 14	108 3	110·3 6	172 3	179 3	−7·7	−0·8	120 2	130 2	11·9
$NiSO_4.6D_2O$ O'Connor & Dale (1966)	0·929 D 17	0·998 D 17	2·686 13	2·814 *W* 13	1·772 16	1·830 16	2·016 Ni 9	113 2	120·0 4	167 1	168 1	−11·6	−9·0	125 1	122 1	3·5
β-$RbMnCl_3.2H_2O$ Jensen & Lehmann (1970)	0·855 29	0·905 20	3·289 Cl 15	3·179 Cl 12	2·477 27	2·282 20	2·221 Mn 20	109 2	102·2 4	159 2	172 2	17·0	−8·1	125 2	127 2	0·9
	0·925 27	0·902 25	3·225 Cl 15 3·469 Cl 12	3·192 Cl 12	2·453 27 2·838 27	2·309 26	2·211 Mn 20	109 2	102·4 3 72·4 2	145 2 127 2	166 2	−34·3 37·4	0·3	127 2	122 2	15·6

Class 1, Type *F*

β-$(COOD)_2.2D_2O$ Coppens & Sabine (1969)	0·945 D 2	0·948 D 2	2·856 2	2·834 2	1·961 2	1·896 2	1·521 D 1	108·7 2	88·0 1	157·3 1	170·4 1	8·0	−0·5	131·4 2	119·8 2	1·4
$\{Ni(C_5H_{11}N_2O)_2H\}^+Cl^-.H_2O$ Schlemper *et al.* (1971)	0·935 6	0·964 6	3·176 Cl 3	3·199 Cl 3	2·269 5	2·240 5	1·896 5	107·8 5	120·4 1	163·4 5	173·8 4	9·9	−4·5	109·9 4	139·7 4	13·7

Class 1, Type *M*

$CsAl(SO_4)_2.12H_2O$ Cromer *et al.* (1966)	0·980 25	0·988 42	2·648 7	2·615 *W* 7	1·688 25	1·653 41	1·883 Al 5	107 3	105·1 2	166 2	164 3	13·7	15·8	121 2	130 2	−13·2
$NaAl(SO_4)_2.12H_2O$ Cromer *et al.* (1967)	0·977 21	0·991 20	2·649 *W* 3	2·624 3	1·673 19	1·636 22	1·881 Al 2	108 2	103·2 1	178 2	174 2	0·2	0·2	124 1	128 1	4·1
$Th(NO_3)_4.5H_2O$ Taylor *et al.* (1966)	0·954 5	0·954 5	2·698 *W* 3	2·698 *W* 3	1·749 6	1·749 6	2·438 Th 4	110·0 5	101·2 1	173·2 6	173·2 6	0·6	−0·6	125·0 3	125·0 3	0
	0·970 5	0·960 5	2·697 *W* 4	2·954 3	1·728 5	1·999 5	2·474 Th 2	111·1 4	107·8 1	177·5 3	173·5 4	−2·3	−5·2	124·9 3	123·3 4	7·4
$UO_2(H_2O)_2(NO_3)_2$ Kent Dalley *et al.* (1971)	0·961‡ 5	0·952 4	2·925 2	2·900 2	1·964 5	1·983 4	2·457 UO_2 1	106·2 4	93·7 1	179·8 1	161·2 5	−0·1	−1·5	120·4 3	124·6 3	26·6
	0·962 5	0·931 5	2·835 2	2·955 3	1·892 5	2·132 6	2·451 UO_2 2	106·3 5	109·4 1	166·1 4	146·8 8	−5·9	29·0	130·4 3	121·0 4	−13·3
$UO_2(NO_3)_2(H_2O)_2.4H_2O$ Taylor & Mueller (1965)	0·975 10	0·971 11	2·706 *W* 8	2·694 *W* 8	1·736 12	1·736 12	2·398 UO_2 3	107·0 8	112·6 2	173 1	168 1	5·6	−11·1	126·9 6	125·9 6	−4·6

Class 1′, Type *J*

$Cu(NH_4)_2(SO_4)_2.6H_2O$ Brown & Chidambaram (1969)	0·964 3	0·963 3	2·826 2	2·822 2	1·872 3	1·871 3	2·230 Cu 1	109·4 3	118·0 1	170·2 3	168·8 2	−5·8	−9·2	112·1 2	114·1 2	47·3
	0·978 3	0·979 3	2·707 2	2·744 2	1·730 3	1·766 3	2·073 Cu 1	105·9 2	104·2 1	178·2 1	177·5 1	−0·8	−2·3	116·9 2	114·2 2	44·4
	0·981 3	0·977 3	2·733 1	2·684 2	1·761 3	1·715 3	1·966 Cu 1	105·7 2	99·0 1	170·5 2	171·3 2	3·9	−8·5	114·5 2	118·5 2	42·3
$CuSO_4.5H_2O$ Bacon & Curry (1962)	0·96	0·94	2·83	2·76 *W*	1·91	1·81	1·986 Cu	111	121	168	170	8·0	−8·6	117·2	113·9	−40·2
	0·96	1·00	2·79	2·76 *W*	1·89	1·76	1·983 Cu	109	130	154	172	6·2	−5·3	112·5	120·1	41·1
$Mn(HCO_2)_2.2H_2O$ Kay *et al.* (1968)	0·987 32	0·979 33	2·711 20	2·764 19	1·771 32	1·785 33	2·208 Mn 13	109 3	113·9 6	158 3	178 3	20·3	2·4	105 2	102·8 8	54·6
$NiSO_4.6D_2O$ O'Connor & Dale (1966)	0·969 D 21	0·967 D 13	2·774 11	2·744 13	1·871 20	1·793 16	2·070 Ni 7	108 2	124·1 4	154 2	167 1	21·8	−3·1	115 1	122 1	36·1

Table 1 (*cont.*)

Class 1′, Type *K*

α-(COOH)$_2$.2H$_2$O	0·964	0·957	2·865	2·881	1·918	1·979	1·480	105·9	83·4	166·9	156·5	−1·7	−12·1	119·9	112·8	42·5
Sabine *et al.* (1969)	5	6	3	3	4	5	4	4	1	4	5			4	3	
α-(COOD)$_2$.2D$_2$O	0·955	0·954	2·880	2·905	1·939	2·008	1·493	105·7	83·5	167·8	156·1	−1·5	12·5	113·7	119·4	42·2
Coppens & Sabine (1969)	D 2	D 2	2	2	2	2	D 2	2	1	2	1			1	1	

* H1 is given by the author as not engaged in hydrogen bonds.

† According to the author H1 is involved in only one hydrogen bond.

‡ In the original paper this water molecule is said to be free from hydrogen bonds.

Distribution of distances and angles

Normality of the histograms in Fig. 2 was tested by comparing the values of the observed frequencies (O_i) with those calculated (E_i) from the estimated mean $\bar{x}$ and variance $\hat{\sigma}^2$ (*cf.* Cooper, 1969).

Calculated distributions, $\bar{x}$, $\hat{\sigma}$ and the quantity:

$$\varphi^2 = \sum_{i=1}^{k} \frac{(O_i - E_i)^2}{E_i}, \qquad (1)$$

which is an estimate of the goodness of fit, are reported in Fig. 2. The values of $\bar{x}$ and $\hat{\sigma}$ are: 0·956 (2), 0·024 (1); 2·810 (9), 0·11 (6); 1·878 (12), 0·14 (1); 107·8 (3), 2·95 (22) and 110·5 (1·5), 14·0 (1·1) for *W*–H, *W*···O, H···O, φ and φ_1 respectively. φ^2 is χ^2-distributed (Cooper, 1969) and, in a strict statistical sense, the values found indicate that the fits to normal distributions are only approximate; this could be ascribed to the smallness of the sample. H···H also tends to be distributed (not reported) around an average value of 1·56 Å within a range 1·65–1·48 Å.

The assignment of a + or − sign to γ would specify the position above or below the π plane. However, since the structures are referred to uncorrelated reference systems, we can use only the modulus of γ; a sign applied to angles in Tables 1 and 2 is significant within that molecule only. We tried to provide α with a + or − sign, according to the inequality $\varphi_1 \gtrless \varphi$ but, since the distortion is not confined to the π plane, the results were ambiguous.

Correlations between bond and angle values

Of the several correlations (usually monotonic) between the geometrical features of the water molecule, *e.g.* (i) *W*–H and H···O, (ii) *W*–H and *W*···O (*cf.* Hamilton & Ibers, 1968) and between (iii) α and *W*···O (Hamilton, 1962), some are supported by semi-empirical potential functions (Chidambaram & Sikka, 1968; Chidambaram, 1968). We find that (i) [Fig. 3(*a*)] and (ii) [Fig. 3(*b*)] are linear with correlation coefficient ϱ (*cf.* Cooper, 1969) equal to −0·44 and −0·55 respectively; we also find linear correlation between H···O and *W*···O [Fig. 3(*c*)], $\varrho = 0·95$, and between φ and φ_1 [Fig. 3(*d*)], $\varrho = 0·55$. The equations and e.s.d.'s of the coefficient, in parentheses, computed by a least-squares procedure, are reported in the corresponding figures. Some further approximate correlations were noted.

(1) γ increases as α deviates from 180°; $\varrho = -0·61$.

(2) γ is often high when either *W*···O or H···O have an average length.

(3) α tends to 180° as φ_1 approaches its average value (110·5°); for $\varphi_1 \gtrless 110·5°$ α diverges appreciably from 180°, but the more distorted hydrogen bonds correspond to $\varphi_1 > \varphi$.

(4) α deviates from 180° as H···O ($\varrho = -0·50$) and *W*···O ($\varrho = -0·29$) increase; this corresponds point (iii) above.

Table 2. *Distances* (Å) *and angles* (°) (*e.s.d.'s below*) *characterizing*

Case of more than one atom coordinated by *W*.

Class 2, Type *A*

	W–H1	*W*–H2	*W*···A1	*W*···A2	H1···A1	H2···A2	*W*···C2	*W*···C3
$K[Au(CN)_4].H_2O$	0·917	0·877	2·943	3·142	2·084	2·269	2·845	2·881
Bertinotti & Bertinotti (1970)	18	27	N 12	N 12	19	25	K 24	K 21
$LiClO_4.3H_2O$	0·932	0·932	2·896	2·896	2·104	2·104	2·170	2·076
Datt *et al.* (1968)							Li	Li
$Na_2HAsO_4.7H_2O$	0·94	0·93	2·743	2·787	1·81	1·85	2·444	2·357
Ferraris *et al.* (1971*b*)	4	3	6	6	4	4	Na 5	Na 5
	0·92	0·99	2·793	2·855	1·87	1·88	2·482	2·464
	3	2	6	6	3	2	Na 5	Na 5
	0·94	1·00	2·995	2·888	2·11	1·95	2·484	2·407
	5	4	6	6	5	5	Na 5	Na 5
	0·93	0·95	2·817	2·840	1·94	1·92	2·383	2·411
	2	3	6	6	2	3	Na 5	Na 5
	0·94	0·94	2·884	2·853	1·95	1·92	2·457	2·441
	2	3	6	6	2	3	Na 5	Na 5
$Na_2Al_2Si_3O_{10}.2H_2O$	0·984	0·943	2·842	3·008	1·875	2·130	2·379	2·382
Torrie *et al.* (1964)	15	16	11	11	15	17	Na13	Na14
$Na_2(H_2SiO_4).5H_2O$	1·005	0·924	2·902	2·851	1·922	1·937	2·470	2·346
Williams & Dent Glasser (1971)	14	13	*W* 9	8	14	13	Na13	Na11
	0·894	0·972	3·134	2·741	2·243	1·777	2·370	2·371
	14	13	9	8	13	13	Na11	Na14
$Na_2S_2O_3.5H_2O$	0·96*	0·95	2·77	2·81	1·82	1·90	2·51	2·34
Padmanabhan *et al.* (1971)	3	2	2	1	4	2	Na2	Na2
	0·94*	0·92	2·73	3·30	1·88	2·52	2·36	2·46
	5	3	*W* 2	S 1	3	2	Na2	Na2
	0·93*	0·93	3·13	2·79	2·38	1·88	2·62	2·44
	3	2	S 2	*W* 2	4	3	Na3	Na2
				3·080		2·287		
				8		18		
$Na_2[Ru(NO_2)_4(NO)(OH)].2H_2O$	0·929†	0·912	2·920	2·973	2·225	2·412	2·613	2·335
Simonsen & Mueller (1965)	17	14	9	8	26	20	Na 6	Na 5
							Class 2, Type *B*	
$BaCl_2.2H_2O$	0·968	0·974	3·182	3·130	2·237	2·173	2·841	2·851
Padmanabhan *et al.* (1963)			Cl	Cl			Ba	Ba
				3·303		2·661		
				Cl				
	0·965	0·954	3·179	3·239	2·223	2·492	2·866	2·894
			Cl	Cl			Ba	Ba
$Fe_3(PO_4)_2.4H_2O$ (4·2°K)	0·970	1·030	2·680	2·546	1·827	1·520	2·169	2·265
Abrahams (1966)	17	10	7	5	15	9	Fe 5	Fe 5
	1·014	0·995	2·644	2·743	1·633	1·793	2·318	2·198
	18	9	7	5	17	9	Fe 5	Fe 5
							Class 2, Type *E*	
$CuSO_4.5H_2O$	0·97	0·96	2·79	2·99	1·84	2·07	1·81	1·76
Bacon & Curry (1962)								
$MgSO_4.7H_2O$	0·962	0·959	2·820	2·903	1·892	1·980	1·803	1·842
Ferraris *et al.* (1972*d*)	9	9	6	*W* 6	9	9	9	9
$(NH_4)_2C_2O_4.H_2O$	0·969	0·969	2·796	2·796	1·843	1·843	1·877	1·877
Padmanabhan *et al.* (1965)								
$Th(NO_3)_4.5H_2O$				2·946		2·067		
Taylor *et al.* (1966)				4		7		
	0·954†	0·983	2·902	3·096	1·963	2·414	1·749	1·728
	7	8	4	4	7	8	6	5
$UO_2(NO_3)_2(H_2O)_2.4H_2O$	0·977	0·933	2·919	2·761	1·943	1·853	1·736	1·850
Taylor & Mueller (1965)	11	13	5	*W* 9	9	14	12	14
	0·947	0·872	2·998	2·702	2·180	1·850	1·736	1·853
	14	14	6	*W* 9	13	14	12	14
							Class 2, Type *G*	
$CsAl(SO_4)_2.12H_2O$	0·947	0·961	2·822	2·766	1·896	1·814	1·653	3·367
Cromer *et al.* (1966)	25	25	7	7	25	27	38	Cs 5
$K[B_5O_6(OH)_4].2H_2O$	0·983	0·927	2·874	2·845	1·893	1·925	1·706	3·006
Ashmore & Petch (1969)	19	18	8	8	21	18	12	K 2
$Li_2SO_4.H_2O$	0·949	0·920	2·871	2·947	1·994	2·111	2·111	1·914
Smith *et al.* (1968)	20	23	6	*W* 10	12	24	24	Li 8
$Na_2HAsO_4.7H_2O$	0·93	0·99	2·819	2·754	1·90	1·81	1·92	2·372
Ferraris *et al.* (1971*b*)	4	3	6	6	4	3	3	Na 5
	0·99	0·94	2·878	2·852	1·90	1·92	1·74	2·352
	4	3	6	*W* 6	4	3	3	Na 5

the water molecule and its environment in crystalline hydrates
The meaning of the symbols is shown in Fig 1.

φ	φ_1	α_1	α_2	γ_1	γ_2	ε	ε_2	ε_3	ψ	ω_1	ω_2
113	110·1	156	175	−22·8	0·3	135·4	53·4	−77·7	81·4	62·8	49·9
2	4	2	3			7					
102·5	128·0	158·0	158·0	10·1	10·1	79·3	39·6	−39·6	90·0	51·2	51·2
104	117·3	171	167	−5·8	−1·8	93·2	−49·2	42·8	81·6	57·0	46·9
3	2	3	3			2					
104	111·6	176	168	4·4	−2·1	81·8	−41·7	39·8	85·7	61·1	42·6
2	2	6	2			2					
110	142·8	168	156	4·0	−0·3	94·9	42·6	−50·7	80·8	52·9	57·0
4	2	4	3			2					
109	133·0	159	163	−4·3	−4·4	85·0	30·0	−54·2	84·8	63·9	44·7
2	2	2	2			2					
107	101·0	169	176	−4·3	−3·8	82·8	−44·4	36·5	79·0	66·6	40·6
2	2	3	4			1					
108	134·2	167	154	1·3	−3·4	100·1	46·8	−49·8	77·0	53·9	54·2
1	3	2	1			4					
101	84·3	164	170	1·0	−4·4	111·2	62·9	−47·2	83·4	70·2	30·7
1	2	1	1			4					
106	108·9	175	171	3·2	8·6	88·6	−38·7	47·1	77·1	46·6	58·9
1	2	1	1			4					
106	105·7	171	163	—	—	—	—	—	—	—	—
3	7	2	2								
108	103·4	159	143	—	—	—	—	—	—	—	—
2	5	3	2								
108	112·9	143	167	—	—	—	—	—	—	—	—
3	6	2	4								
109 2	159·2 3 97·9 2	131 2	145 2 120 2	−11·6	24·6 −5·8	99·6 2	−57·2	40·4	80·4	70·8	78·7
105·8	111·2	165·4	167·3	−14·6	11·3	122·9	61·7	−60·2	84·4	52·8	53·0
102·5	99·4 76·5	171·0	135·1 125·1	2·5	54·0 −33·1	117·4	60·2	−57·2	89·9	41·8	60·7
111	107	145	173·7	34·0	−6·2	94·9	42·0	−44·9	68·8	57·0	54·4
1	2	1	9			2					
104·4	92·6	176·5	158·3	3·5	12·8	126·3	64·1	−59·7	81·0	55·6	49·2
9	2	6	8			2					
106	122	167	161	11·6	−1·3	112·6	−56·6	54·2	81·9	50·6	55·0
106·2	101·5	161·8	161·0	−17·4	−18·7	96·3	26·9	−69·4	89·5	35·0	60·0
8	2	8	8								
110·3	125·0	167·2	167·2	−6·1	5·7	123·1	62·0	−60·9	87·7	55·2	55·1
106·9 7	121·7 1 82·2 1	168·0 6	147·9 6 126·0 5	12·0	16·6 −49·1	107·2 3	59·4	−47·8	88·0	46·7	60·2
107	134·4	177	164	−2·2	−15·5	98·6	37·2	−60·7	84·2	61·6	45·2
1	2	1	1			6					
115	140·4	144	165	14·2	11·4	104·3	−38·5	65·7	88·8	62·9	51·7
1	2	1	1			6					
107	97·1	166	171	9·7	8·1	90	49·8	−40·3	89·9	59·9	48·2
2	2	2	2			1					
108	114·2	176	172	−3·3	3·4	105·1	−60·8	44·2	89·1	50·6	57·6
1	3	1	1			5					
111	146·5	153	151	−12·3	−0·2	93·3	−58·4	31·9	77·7	57·5	53·2
1	2	1	1			5					
110	127·0	171	160	−4·1	−9·2	97	60·2	33·9	82·1	35·5	75·0
3	2	3	2			1					
110	116·9	175	175	2·4	−1·9	106	65·2	−40·6	84·8	63·2	47·0
3	9	3	3			1					

Table 2

$NaAl(SO_4)_2.12H_2O$	0·972	0·998	2·822	2·649	1·908	1·783	1·673	2·453
Cromer *et al.* (1967)	25	26	3	3	26	27	21	Na2
$Na_2(H_2SiO_4).5H_2O$	1·007	0·962	2·654	2·995	1·650	2·034	1·79	2·449
Williams & Dent Glasser (1971)	13	13	8	*W* 8	13	13	1	Na14
$Na_2S_2O_3.5H_2O$	0·98*	0·98	2·73	2·94	1·76	1·97	1·88	2·45
Padmanabhan *et al.* (1971)	2	3	2	2	2	3	3	Na4
	0·95*‡	0·96	—	3·400	2·59	2·59	1·88	2·64
	2	3		S 9	2	3		Na3
							Class 2, Type *H*	
$CaHAsO_4.2H_2O$	0·97	0·99	2·741	2·799	1·78	1·82	2·18	2·430
Ferraris *et al.* (1971*a*)	2	3	11	13	2	2	3	Ca 9
$CaHPO_4.2H_2O$	0·972	0·978	2·782	2·757	1·812	1·784	2·160	2·427
Curry & Jones (1971)	9	13	6	10	8	12	17	Ca 6
$Cd(NO_3)_2.4D_2O$	0·966	0·963	2·946	2·865	2·004	1·918	1·952	2·295
McDonald & Sikka (1969)	D 15	D 18	15	16	15	15	D 19	Cd13
$MgSO_4.7H_2O$	0·985	0·961	2·734	2·728	1·758	1·772	1·980	2·109
Ferraris *et al.* (1972*d*)	9	9	6	6	9	9	9	Mg 5
	0·972	0·959	2·923	2·756	1·965	1·804	1·961	2·096
	9	9	6	*W* 6	9	9	9	Mg 5
$MgSO_4.4H_2O$	0·958§	0·981	2·831	2·734	1·902	1·754	2·419	2·073
Baur (1964)	12	10	5	6	11	10	13	Mg 5
$MnCl_2.4H_2O$	0·971	0·964	3·169	2·923	2·202	1·969	2·014	2·219
El Saffar & Brown (1971)	2	2	Cl 1	*W* 1	2	2	3	Mn 1
				3·282		2·500		
	0·967	0·944	3·174	Cl 1	2·228	3		
	2	3	Cl 1	3·295	2	2·636	1·969	2·223
				Cl 1		3	2	Mn 3
$NiSO_4.6D_2O$	0·965	0·968	2·837	2·749	1·938	1·798	1·830	2·099
O'Connor & Dale (1966)	D 17	D 17	12	13	16	18	D 16	Ni 9
							Class 3, Type *Q*	
$Na_2(H_2SiO_4).5H_2O$	0·953	0·925	2·736	2·744	1·786	1·821	1·922	2·445
Williams & Dent Glasser (1971)	13	14	9	9	13	6	14	Na13
	0·950	0·940	2·744	2·631	1·790	1·692	2·034	2·554
	13	13	W 9	8	13	13	13	Na11
							Class 4, Type *L*	
$K_2C_2O_4.H_2O$	0·963‖	0·963	2·754	2·754	1·802	1·802	2·907	2·907
Sequeira *et al.* (1970)	2	2	1	1	3	3	K 2	K 2

* The atomic coordinates given in the original paper are partly incorrect (Padmanabhan, 1972); therefore only the bond distances and angles reported by the authors, which are claimed to be correct, are given here.

† The possibility of a bifurcated hydrogen bond is not considered by the authors.

‡ This water molecule is wrongly classified as type *E* in the original paper; H1 is probably engaged in a hydrogen bond with a sulphur atom [*cf.* (4)].

§ If the asterisked water molecule is involved in only one hydrogen bond, this water molecule would belong to the type *H* (class 2).

‖ Two potassium atoms 'tetrahedrally coordinated' are at 3·34 Å from *W* ($\angle$K–*W*–K = 144°).

(5) If $\varphi_1 > \varphi$, $W\cdots O$ tends to increase with increasing φ_1; if $\varphi_1 < \varphi$, the values of $W\cdots O$ are random.

Discussion

Average water molecule

The distributions reported in Fig. 2 generally have standard deviations $\hat{\sigma}$ greater than the e.s.d.'s of the corresponding distances or angles. We conclude that the distribution is meaningful and is due to crystallochemical causes; further we believe that under 'standard conditions' a water molecule in crystalline hydrates will assume the average situation reflected in the histograms, *i.e.* planar group for H_2O plus two acceptors, $W\text{–}H \simeq 0{\cdot}96$ Å, $\varphi_1 \simeq \varphi \simeq 108°$, $W\cdots O \simeq 2{\cdot}81$ Å, $H\cdots O \simeq 1{\cdot}88$ Å, coordinated cations along the two (or only one) lone-pair orbitals or their bisector. The resulting average water molecule is closely similar to the conformation of this molecule found in the vapour state except that the usual 'tetrahedral' environment of the water molecule in the solid state enlarges the H–*W*–H angle.

Influence of an unbalanced distribution of bond strength

Undoubtedly, electrostatic forces strongly influence the geometry of the water hydrogen bond, as shown, for example, by the effectiveness of Baur's (1965, 1972) electrostatic theory in predicting the position of hydrogen atoms in crystalline hydrates. On the other hand most of the structures considered are sufficiently

(*cont.*)

102·6 2	95·7 1	156 2	162 2	5·1	−12·7	125·1 7	62·1	−61·8	83·9	36·3	66·3
103 1	106·3 3	175 1	179 1	0·6	0·7	110·2 5	−57·2	51·5	82·7	58·5	44·0
108 2	101·8 4	171 2	173 2	—	—	—	—	—	—	—	—
110 3	—	—	145 2	—	—	—	—	—	—	—	—
106 3	103·3 4	176 3	174 2	−4·4	−4·6	131	−79·3	31·8	85·4	43	62·8
107 1	104·0 3	176 1	173 1	−3·2	−2·5	129·0 4	−75·3	24·9	85·6	45·1	61·6
105 1	103·1 4	165 1	168 1	−5·5	0	103·5 7	50·4	−53·0	87·6	41·7	42·0
106·9 8	97·2 2	170·9 8	173·1 8	1·8	−3·4	103·6 8	−63·5	38·2	−86·5	52·6	54·3
109·5 8	121·9 2	168·0 8	172·1 8	4·9	−1·8	108·0 8	−41·6	64·4	81·2	60·4	49·2
109 1	114·3 2	163 1	178 1	15·5	1·4	116·8 3	84·7	−22·9	86·1	56·5	52·1
106·1 2	112·3 1	174·1 2	170·4 2	3·0	8·5	105·0 1	−60·9	43·7	86·1	60·5	45·6
104·3 3	76·9 1 126·8 1	165·7 2	140·3 2 127·4 2	−12·5	19·0 −25·1	110·5 1	−74·6	45·9	88·6	52·5	51·8
110 2	131·4 4	154 2	167 1	11·7	−9·2	106·6 6	−59·1	45·8	81·6	48·2	61·5
113 1	117·6 3	175 1	177 1	2·1	−2·0	164·3 6	74·6	−89·3	89·4	81·5	14·8
			$W\cdots Cl=2{\cdot}445$; Na13		$\varepsilon_1=-11{\cdot}1$;	$\delta_1=115{\cdot}7$; 9		$\delta_2=129{\cdot}6$; 9			
108 1	109·2 3	179 1	179 1	1·1	−0·5	160·4 6	−86·2	73·6	88·2	33·9	74·1
			$W\cdots Cl=2{\cdot}486$; Na14		$\varepsilon_1=1{\cdot}5$;	$\delta_1=100$; 1		$\delta_2=145{\cdot}5$; 9			
107·6 2	118·8 1	169·7 3	169·7 3	−5·9	5·9	89·1 1	−7·8	7·8	11·1	54·6	53·0

ionic for Pauling's rules to be relevant. However, except in simple structures, his second rule, in particular, is not usually satisfied. An unbalanced distribution of the bond strength p would clearly produce local strain in the structure which, in order to minimize its energy, will assume a packing with local distortions ('non-standard conditions').

The flexibility of water geometry and of its environment in a crystal structure enables the whole structural group to act as a 'strain-absorber'; consequently, a 'quasi-normal' distribution of bonds and angles results since the requirements of distortions will be randomly distributed over a large number of structures. Further, the observed linear correlations may be justified on the basis of an unbalanced distribution of bond strengths.

Baur (1970) [*cf.* also Baur (1972) and Khan & Baur (1972)] states that 'the lengths (O···O) of hydrogen bonds vary inversely with the difference ($\Delta p = p_{\text{donor}} - p_{\text{acceptor}}$) of the p values received by the donor and the acceptor atoms of the hydrogen bonds'; the correlation of the experimental values is satisfactorily linear. A linear correlation between O–H and Δp (not reported) affirms the validity of Baur's statement that the larger is Δp (positive), the longer will be O–H; a similar correlation must be valid for H···O.

Since all the quantities are linearly correlated to Δp, the existence of the correlations of Fig. 3(*a*), (*b*) and (*c*) appears to be justified crystallochemically; the hydrogen atom moves from its 'average position' towards the underbonded oxygen atom to compensate the difference Δp between donor and acceptor. The 'average position' corresponds to $\Delta p = 0$; for such a value O–H, W···O and H···O generally have just the mean values reported in the histograms.

Other correlations

Calculations of the energy associated with hydrogen bonds show (*cf.* Murrell, 1969) that they are intermediate between covalent and van der Waals interactions. Furthermore (Chidambaram, 1962), the bending of hydrogen bonds requires less energy than a distortion of the H–O–H angle, and long hydrogen bonds are stable only if bent. Such considerations agree with the correlations (3), (4) and (5).

Large φ_1's, due to the rigidity of part of the structure, are likely to require long hydrogen bonds even with moderately negative Δp's; in fact [*cf.* Fig. 6 of Baur (1970)] large O···O values are found for a wide range of Δp and, on the other hand, *W*···O tends to increase with φ_1 [point (5)].

Since a linear hydrogen bond is energetically the most favourable (*cf.* Chidambaram & Sikka, 1968), one can understand the linear correlation [Fig. 3(*d*)] between φ_1 and φ, even if φ follows φ_1 very slowly, in agreement with the large energy required for its distortion.

Strong (=short) and linear [point (1)] hydrogen bonds seem to favour the planarity of the group comprising H_2O and two acceptor atoms even if sometimes this planarity does not occur in order that hydrogen bonds of typical length may be established [point (2)].

Lower and upper limits of the W···O hydrogen bond

According to the calculations of Chidambaram & Sikka (1968) and Chidambaram (1968), when *W*···O >3 Å any amount of bending could be tolerated but, beyond a certain value of bending, the van der Waals repulsion between the oxygen atoms surpasses the cohesion due to the hydrogen atom; *W*···O = 3 Å would require H···O ≃ 2 Å. The correlations of Fig. 3(*a*), (*b*) and (*c*), however, support the existence of hydrogen bonds with H···O 2·2 Å or perhaps 2·3 Å long. In doubtful cases, one should check whether *W*, H and the acceptors conform to configurations characteristic of hydrogen bonds. If the position of H is not known, one must consider the *W*···O length. Fig. 3(*b*) and (*c*) shows that this length should not exceed 3·1 Å or, exceptionally, 3·2 Å; the limiting cases often correspond to bifurcated hydrogen bonds.

The *W*···O distance was never found to be shorter than 2·6 Å (H···O about 1·65 Å long); the more usual values are between 2·7 and 2·9 Å, the region of weak (*cf.* Sokolov, 1965) hydrogen bonds.

Peculiarities of the W···O hydrogen bond

In terms of potential functions (Blinc, Hadži & Novak, 1960) short hydrogen bonds imply two minima which, with the shortening of the bond, become symmetric and separated by a smaller barrier. Clearly the water molecule cannot share its hydrogen atoms beyond a certain point without losing its character.

It seems to be a peculiarity of the *W*···O hydrogen bonds to link layers corresponding to cleavage surfaces, while other O···O bonds are inside such layers contributing to their stability.

The straight lines of Fig. 3 are valid only for the intervals shown, *i.e.* for weak hydrogen bonds, and will fail for quasi-symmetrical or symmetrical bonds (*cf.* a special case in Ferraris, Jones & Yerkess, 1972*c*), which even require correlation with opposite sign. Such a distinct behaviour clearly supports those models according to which the ratio of different terms of bond energy varies with bond strength (*cf.* Murrell, 1969; Sandorfy, 1970; Sokolov, 1965).

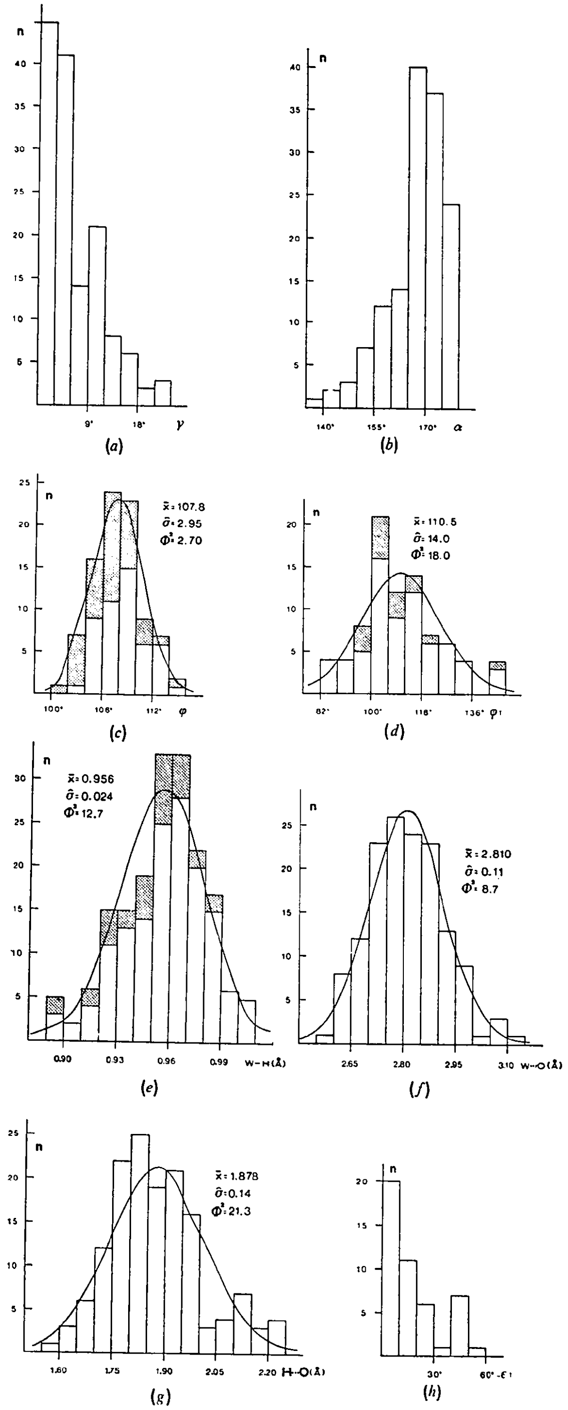


Fig. 2. Histograms showing quantities characterizing the hydrogen-bonded systems reported in Tables 1 and 2. Dotted areas correspond to the cases where *A* is not an oxygen atom [(*d*) and (*e*)] or *W* coordinates more than one cation (*c*). The superimposed curve represents the frequencies calculated on the assumption of normal distributions with mean $\bar{x}$ and standard deviation $\hat{\sigma}$ given beside the histogram.

Classification of the hydrate water molecules

A generally accepted classification of the hydrate water molecules based on the coordination of the lone-pair orbitals has been proposed by Chidambaram, Sequeira & Sikka (1964) and slightly modified by Hamilton & Ibers (1968). While confirming the validity of previous approaches to the problem, our result suggests the need for a revised classification to take into account water molecules coordinating M^{n+} ($n>2$) cations, or more than two cations, or cations in positions intermediate between a lone-pair orbital and the bisector of the lone-pair orbitals. In its five classes, this new system (Table 3) incorporates the types proposed earlier by Chidambaram *et al.* (1964).

Class 1

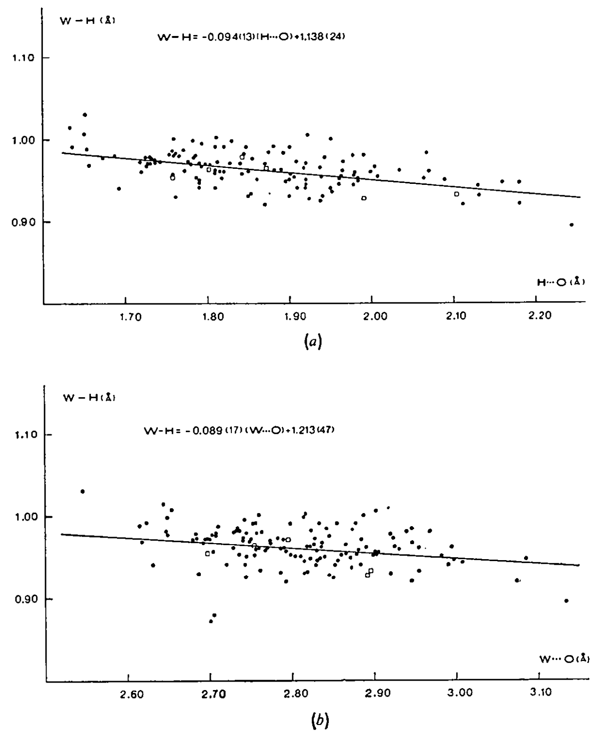
W coordinates only one cation which tends to be along the bisector (*cf.* δ_1 and δ_2 in Table 1) of the lone-pair orbitals; since [Fig. 2(*h*)] the values of ε_1 show a gap about between 27 and 40°, the upper value of ε_1 for this class should be around 25–30°.

Class 1′

W coordinates only one cation along a lone-pair orbital (*cf.* δ_1 and δ_2 in Table 1); ε_1 is around 45°. For classes 1 and 1′ the value of the $C1\cdots W$–H angle (δ) coincides, within a few degrees, with that of the corresponding $C1\cdots W\cdots A$ angle (not reported).

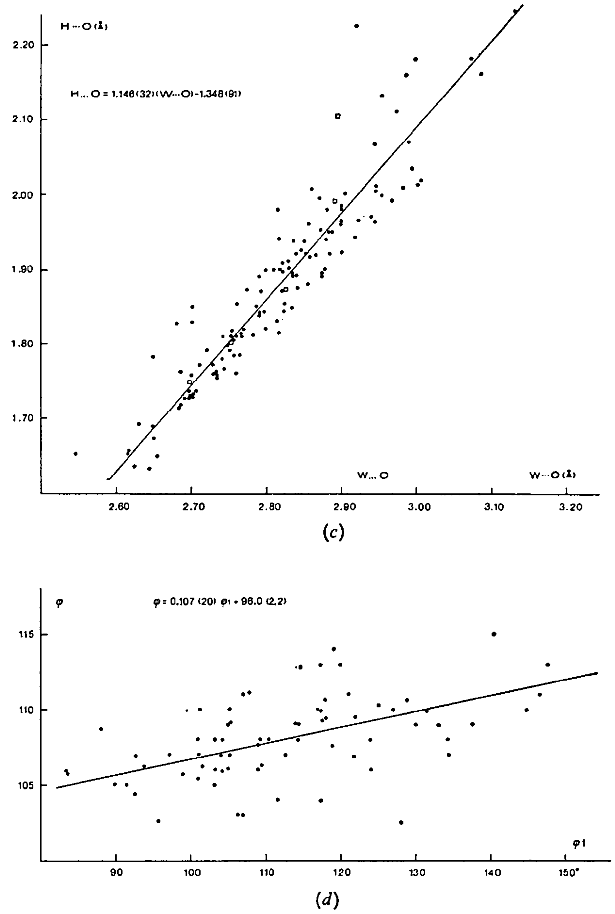
Table 3. *Classification of the water molecules in the crystalline hydrates*

	Type	*C*1	*C*2	*C*3
Class 1 *C*1 approximately along the bisectrix of the lone-pair orbitals	*C*	M^+	–	–
	D	M^{2+}	–	–
	F	H	–	–
	M	M^{n+}	–	–
Class 1′ *C*1 along a lone-pair orbital	*I*	M^+	–	–
	J	M^{2+}	–	–
	K	H	–	–
	N	M^{n+}	–	–
Class 2 *C*2 and *C*3 along the lone-pair orbitals	*A*	–	M^+	M^+
	B	–	M^{2+}	M^{2+}
	E	–	H	H
	G	–	M^+	H
	H	–	M^{2+}	H
Class 3 *C*1 approximately in π plane, *C*2 and *C*3 perpendicular to π	*O*	M^+	M^+	M^+
	P	H	M^+	M^+
	Q	M^+	M^+	H
	R	M^+	H	H
	S	H	H	M^+
	T	H	H	H
Class 4	*L*	Coordination not specifically directed		



(*a*)

(*b*)



(*c*)

(*d*)

Fig. 3. Experimental points (squares are for multiple points) and least-squares straight lines, with their equation, for pairs of linearly dependent quantities in $W\cdots$O hydrogen bonds.

Class 2

Along the two lone-pair orbitals of W there are two cations which, according to the known crystal structures, can be H, M^+ or M^{2+}. Usual values for ε_2 and ε_3 are around 50°, but A and E types prefer values smaller and larger than 50°, respectively. Quite often ε_2 is appreciably different from ε_3, particularly in the case of E, G and H types; while G and H types usually show values of ε larger than 100°, A, E and B types prefer values <90, $\simeq 90$ and $>90°$, respectively. π_1 and π planes are, in first approximation, perpendicular; type B shows the largest deviations of ψ from 90°. The intersection between π_1 and π corresponds, in first approximation, to the bisector of the H–W–H angle (*cf.* the values of ω_1 and ω_2 in Table 2) and, according to calculations not reported, to the bisector of the $A\cdots W\cdots A$ (φ_1) angle.

Class 3

W coordinates three cations; one tends to lie in the π plane, while the others are nearly perpendicular to the same plane in such a way that the coordination polyhedron around W is essentially a trigonal bipyramid. From known crystal structures, it appears that this kind of coordination is possible only with hydrogen and alkali atoms; if so, six types (Table 3) would be possible, of which three (O, Q and R) have been found so far (*cf.* also Ibers, Hamilton & MacKenzie, 1964).

Class 4

No cations are specifically directed along the lone-pair orbitals or their bisector, or are at least near a plane containing W and orthogonal to π.

This classification, like its predecessors, is essentially a summary of the different situations the water molecule may face; as with the criteria published by Baur (1972) when the present paper was completed, it must be taken into account for predicting hydrogen bonds in the absence of unambiguous location of the hydrogen atoms. The question of the systematic influence of the position and nature of the cations on the water molecule geometry is still open (Chidambaram *et al.*, 1964; Chidambaram & Brown, 1965; Coppens & Sabine, 1969; Hamilton & Ibers, 1968). In particular, it seems that large H–W–H angles are not confined to transition-metal hydrates [*cf.* $CaHAsO_4.H_2O$ (Ferraris, Jones & Yerkess, 1972*a*)] but may be dictated by large $A\cdots W\cdots A$ angles. Further subclassification could take into account the nature of the acceptors (A); differences between acceptors $A1$ and $A2$ can influence the hydrogen-bonding system appreciably.

References

Abrahams, S. C. (1962). *J. Chem. Phys.* **36**, 56.

Abrahams, S. C. (1966). *J. Chem. Phys.* **44**, 2230.

Abrahams, S. C. & Prince, E. (1962). *J. Chem. Phys.* **36**, 50.

Ashmore, J. P. & Petch, H. E. (1969). *Canad. J. Phys.* **47**, 1091.

Atoji, M. & Rundle, R. E. (1958). *J. Chem. Phys.* **29**, 1306.

Bacon, G. E. & Curry, N. A. (1962). *Proc. Roy. Soc.* A**266**, 95.

Baur, W. H. (1964). *Acta Cryst.* **17**, 863.

Baur, W. H. (1965). *Acta Cryst.* **19**, 909.

Baur, W. H. (1970). *Trans. Amer. Cryst. Assoc.* **6**, 129.

Baur, W. H. (1972). *Acta Cryst.* B**28**, 1456.

Bertinotti, C. & Bertinotti, A. (1970). *Acta Cryst.* B**26**, 422.

Blinc, R., Hadži, D. & Novak, A. (1960). *Z. Elektrochem.* **64**, 567.

Brown, G. M. & Chidambaram, R. (1969). *Acta Cryst.* B**25**, 676.

Chidambaram, R. (1962). *J. Chem. Phys.* **36**, 2361.

Chidambaram, R. (1968). *Proc. Nucl. Phys. Solid State Phys. Symposium, Bombay*, p. 215.

Chidambaram, R. & Brown, G. M. (1965). *Chem. Div. Ann. Prog. Rep. ORNL*, p. 121.

Chidambaram, R., Navarro, Q. O., Garcia, A., Linggoatmodjo, K., Lin Shi-Chien, Il-Hwan Suh, Sequeira, A. & Srikanta, S. (1970). *Acta Cryst.* B**26**, 827.

Chidambaram, R., Sequeira, A. & Sikka, S. K. (1964). *J. Chem. Phys.* **41**, 3616.

Chidambaram, R. & Sikka, S. K. (1968). *Chem. Phys. Letters*, **2**, 162.

Cooper, B. E. (1969). *Statistics for Experimentalists.* Braunschweig: Pergamon Press.

Coppens, P. & Sabine, T. M. (1969). *Acta Cryst.* B**25**, 2442.

Cromer, D. T., Kay, M. I. & Larson, A. C. (1966). *Acta Cryst.* **21**, 383.

Cromer, D. T., Kay, M. I. & Larson, A. C. (1967). *Acta Cryst.* **22**, 182.

Curry, N. A. & Jones, D. W. (1971). *J. Chem. Soc.* (*A*), p. 3725.

Datt, I. D., Rannev, N. V. & Ozerov, R. P. (1968). *Sov. Phys. Crystallogr.* **13**, 204.

El Saffar, Z. M. & Brown, G. M. (1971). *Acta Cryst.* B**27**, 66.

Ferraris, G., Jones, D. W. & Yerkess, J. (1971*a*). *Acta Cryst.* B**27**, 349.

Ferraris, G., Jones, D. W. & Yerkess, J. (1971*b*). *Acta Cryst.* B**27**, 354.

Ferraris, G., Jones, D. W. & Yerkess, J. (1972*a*). *Acta Cryst.* B**28**, 209.

Ferraris, G., Jones, D. W. & Yerkess, J. (1972*b*). *Z. Kristallogr.* **135**, 240.

Ferraris, G., Jones, D. W. & Yerkess, J. (1972*c*). *Acta Cryst.* B**28**, 2430.

Ferraris, G., Jones, D. W. & Yerkess, J. (1972*d*). *J. Chem. Soc. Dalton.* In the press.

Hamilton, W. C. (1962). *Ann. Rev. Phys. Chem.* **13**, 19.

Hamilton, W. C. & Ibers, J. A. (1968). *Hydrogen Bonding in Solids.* New York: Benjamin.

Ibers, J. A., Hamilton, W. C. & MacKenzie, D. R. (1964). *Inorg. Chem.* **3**, 1412.

Jensen, S. J. & Lehmann, M. S. (1970). *Acta Chem. Scand.* **24**, 3422.

Kay, M. I., Almodovar, I. & Kaplan, S. F. (1968). *Acta Cryst.* B**24**, 1312.

Kent Dalley, N., Mueller, M. H. & Simonsen, S. H. (1971). *Inorg. Chem.* **10**, 323.

Khan, A. A. & Baur, W. H. (1972). *Acta Cryst.* B**28**, 683.

McDonald, A. C. & Sikka, S. K. (1969). *Acta Cryst.* B**25**, 1804.

MURRELL, J. N. (1969). *Chem. Brit.* **5**, 107.
O'CONNOR, B. H. & DALE, D. H. (1966). *Acta Cryst.* **21**, 705.
PADMANABHAN, V. M. (1972). Private communication.
PADMANABHAN, V. M., BUSING, W. R. & LEVY, H. A. (1963). *Acta Cryst.* **16**, A26.
PADMANABHAN, V. M., SRIKANTA, S. & MEDHI ALI, S. (1965). *Acta Cryst.* **18**, 567.
PADMANABHAN, V. M., YADAVA, V. S., NAVARRO, Q. O., GARCIA, A., KARSONO, L., IL-HWAN SUH & LIN SHI CHIEN (1971). *Acta Cryst.* B**27**, 253.
PETERSON, S. W. & LEVY, H. A. (1957). *J. Chem. Phys.* **26**, 220.
SABINE, T. M., COX, G. W. & CRAVEN, B. M. (1969). *Acta Cryst.* B**25**, 2437.
SANDORFY, C. (1970). *Colloques Internationaux du CNRS. Aspects de la Chimie Quantique Contemporaine*, p. 237. Menton, 1970.
SCHLEMPER, E. O., HAMILTON, W. C. & LA PLACA, S. J. (1971). *J. Chem. Phys.* **54**, 3990.
SEQUEIRA, A., SRIKANTA, S. & CHIDAMBARAM, R. (1970). *Acta Cryst.* B**26**, 77.
SIKKA, S. K. & CHIDAMBARAM, R. (1969). *Acta Cryst.* B**25**, 310.
SIKKA, S. K., MOMIN, S. N., RAJAGOPAL, H. & CHIDAMBARAM, R. (1968). *J. Chem. Phys.* **48**, 1883.
SIMONSEN, S. H. & MUELLER, M. H. (1965). *J. Inorg. Nucl. Chem.* **27**, 309.
SMITH, H. G., PETERSON, S. W. & LEVY, H. A. (1968). *J. Chem. Phys.* **48**, 5561.
SOKOLOV, N. D. (1965). *Ann. Chim.* **10**, 497.
TAYLOR, J. C. & MUELLER, M. H. (1965). *Acta Cryst.* **19**, 536.
TAYLOR, J. C., MUELLER, M. H. & HITTERMAN, R. L. (1966). *Acta Cryst.* **20**, 842.
TORRIE, B. H., BROWN, I. D. & PETCH, H. E. (1964). *Canad. J. Phys.* **42**, 229.
WILLIAMS, P. P. & DENT GLASSER, L. S. (1971). *Acta Cryst.* B**27**, 2269.

Acta Cryst. (1972). B**28**, 3583

The Crystal Structure of $Na_2Mg_2Si_6O_{15}$

BY M. E. CRADWICK AND H. F. W. TAYLOR

Department of Chemistry, University of Aberdeen, Old Aberdeen, Scotland

(*Received* 27 *June* 1972)

The compound $Na_2Mg_2Si_6O_{15}$ is essentially isostructural with tuhualite, $[(Na, K)_2Fe_2^{2+}Fe_2^{3+}Si_{12}O_{30}.H_2O]$. The silicate anions are corrugated ribbons, two tetrahedra wide, and are made up from rings of four tetrahedra fused together. Some of the Mg^{2+} ions are tetrahedrally coordinated, and the structure could alternatively be described as being based on a framework with some of the tetrahedral sites occupied by Mg^{2+} and a 7:15 ratio of tetrahedral cations to oxygen. The remaining Mg^{2+} ions are octahedrally coordinated, and of the Na^+ ions, some have 9 and others 10 oxygen neighbours within 3·1 Å.

Introduction

The compound $Na_2Mg_2Si_6O_{15}$ was first described by Botvinkin, Popova & Manuilova (1937), and crystal data for it were reported by Shahid & Glasser (1972). Cradwick, Shahid & Taylor (1972) published a note on the crystal structure, describing the silicate anion, which they found to be a corrugated ribbon, two tetrahedra wide. This was wrongly described as a new type of silicate anion; Dr S. Merlino has since drawn our attention to the fact that the same anion occurs in the mineral tuhualite, $[(Na,K)_2Fe_2^{2+}Fe_2^{3+}Si_{12}O_{30}.H_2O]$, the structure of which he had determined earlier (Merlino, 1969), and comparison of the two structures shows them to be essentially isostructural. In this paper we report the structure of $Na_2Mg_2Si_6O_{15}$, of which only some features were described in the previous note.

Crystal data

The crystal data, found by Shahid & Glasser (1972) and confirmed by us by powder diffractometry (λ for Cu $K\alpha = 1{\cdot}5418$ Å), were as follows: orthorhombic, *Cmca* or *C2cb*, $a = 14{\cdot}165$, $b = 17{\cdot}59$, $c = 10{\cdot}205$ Å, $V = 2542{\cdot}7$ Å^3, $Z = 8$, $D_x = 2{\cdot}629$ g.cm^{-3}. Our own results show the space group to be *Cmca*. The *a* and *c* axes are here interchanged relative to those used in the earlier reports, to make them the same as those used by Merlino (1969).

Experimental methods, structure determination and refinement

Preparation of single-crystal material is difficult as the compound, which melts incongruently, has so far been obtained only by cooling melts that are both highly viscous and of different composition from itself; Dr F. P. Glasser and Dr K. A. Shahid kindly provided a specimen. It was an irregular fragment, a few tenths of a millimetre in its longest dimension, and consisted of the crystal embedded in a larger amount of glass, from which it could not be separated. Intensity data were collected using an automatic linear diffractometer with Mo $K\alpha$ radiation, except for a few reflexions for which this gave uncertain results, and for which intensities were estimated visually from Weissenberg photographs. In general, the intensities of four equivalent reflexions were averaged to give that of each