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Hydrogen Bonding in Perchloric Acid Hydrates

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A bond-valence analysis of five perchloric acid hydrates shows that normal hydrogen bonds account for only about one half of the bonding of the perchlorate ion. Each H atom also forms an average of four additional weak interactions (H···O acceptor ~2·3 to 3·1 Å; O–H···O ~80 to 120°) which account for the rest of the bonding. A distinction can be made between the normal and the very weak hydrogen bonds in the lower hydrates but this distinction is less clear in the higher hydrates where the distribution of H···O bond strengths tends to form a continuum.

Introduction

Because of its size and low formal charge, the perchlorate ion (ClO_4^-) is not able to bond hydrogen atoms strongly. Consequently in hydrates and aqueous solution it tends to form relatively weak hydrogen bonds (Brink & Falk, 1970*a*,*b*; Sequeira, Bernal, Brown & Faggiani, 1975).

In this paper the character of the bonding around the perchlorate ion in the solid perchloric acid hydrates is analysed using bond valences (Brown & Shannon, 1973). The bond lengths are transformed into bond valences which have the property that the sums of the valences around each atom equal the atomic valence. Such a property provides an internal check on the validity of the method since failure of the bond valences to add correctly means either that the transformation has not been properly performed, that the structure is incorrectly determined or that the technique does not apply. The technique has been shown earlier to work well in oxides (including those involving hydrogen bonds) and is therefore expected to work for the perchloric acid hydrates. As will be shown below, using suitable correlations between bond length and bond valence, good sums can be obtained for the known structures provided that the very long H···O interactions are included.

Treatment of data

The atomic positions were taken from X-ray diffraction studies at low temperature described in the references given in Table 1(*a*) to (*e*). In these studies the hydrogen-atom positions were determined in most cases from residual electron density and chemical considerations. The positions chosen here were altered slightly to correspond to the expected nuclear positions by setting all the O(donor)–H distances between 0·95 and 1·10 Å, the longer distances being used for the strong hydrogen bonds (O–O < 2·7 Å). Although there is considerable uncertainty in the exact positions of the hydrogen atoms, the values of the H···O(acceptor) distances will be accurate to 0·1 Å and O–H···O angles to 10°, an uncertainty that will not invalidate the conclusions drawn below.

Table 1. *Valences of bonds between atoms in perchloric acid hydrates in valence units*

$\sum^1$ = valence sums ignoring bonds less than 0·10 v.u.
$\sum^2$ = valence sums including all bonds.
Numbers in italics were chosen to ensure that sums around H were 1·00 v.u. The values given are those used in calculating $\sum^2$. Different values were used for $\sum^1$ (see text).
Bonds enclosed in a rectangle are multiple hydrogen bonds linking the same donor and acceptor O atoms.
σ = r.m.s. deviation of $\sum^2$ from atomic valence.

(*a*) $HClO_4.H_2O$ (Nordman, 1962)

	H(1)	H(2)	H(3)	Cl	$\sum^1$	$\sum^2$
O(1)	0·03	0·02	0·02	1·88	1·88	1·99
		0·04				
O(2)	0·23	0·01		1·67	1·90	1·95
		0·03	0·01			
O(3)	0·02		0·02	1·73	1·93	2·01
	0·01	0·20				
		0·03				
O(4)	0·01	0·01	0·25	1·64	1·89	1·96
	0·03	0·02				
O(5)	*0·67*	*0·68*	*0·66*		2·30	2·01
$\sum^2$	*1·00*	*1·00*	*1·00*	6·92		σ = 0·04

(*b*) $HClO_4.2(H_2O)$ (Olovsson, 1968)

Hydrogen-atom positions postulated.

	H(1)	H(2)*	H(3)*	Cl	$\sum^1$	$\sum^2$
O(1)		0·17*, 0·02*		1·65	1·99	2·03
O(2)	0·01	0·02*		1·79	1·79	1·87
	0·01		0·01*			
O(3)*	0·01*		0·17	1·81	1·98	2·05
		0·04	0·02			
O(4)*	*0·48**	0·02	0·01		2·16	2·03
		0·02	0·02			
		0·71	*0·77*			
$\sum^2$	*1·00*	*1·00*	*1·00*	7·06		σ = 0·07

* Occurs twice in the molecule.

Table 1 (*cont.*)

(*c*) $HClO_4.2\frac{1}{2}(H_2O)$ (Almlöf, Lundgren & Olovsson, 1971)

	H(11)	H(12)	H(13)	H(21)	H(22)	H(31)	H(32)	H(33)	H(41)	H(42)	H(51)	H(52)	Cl(1)	Cl(2)	$\sum^1$	$\sum^2$
O(11)					0·01	0·03		0·01		0·12			1·89		2·01	2·06
O(12)					0·01							0·15 0·06	1·77		1·92	1·99
O(13)							0·05	0·06	0·16		0·02	0·02	1·70		1·86	2·01
O(14)	0·04		0·04	0·01		0·03	0·02	0·02	0·05	0·02	0·02		1·76		1·76	2·01
O(21)				0·04		0·03	0·01			0·06				1·80	1·80	1·98
										0·04						
O(22)	0·02		0·01	0·19	0·11							0·01		1·66	1·96	2·00
O(23)		0·02	0·01	0·01	0·03			0·01				0·01		1·80	1·80	1·89
					0·01											
O(24)	0·04		0·02			0·02		0·15	0·01		0·02			1·75	1·90	2·01
O(1)	*0·64*	*0·67*	*0·62*	0·01	0·03						0·01	0·01			2·17	2·02
				0·01	0·02											
O(2)	0·01		0·29	*0·73*	*0·78*	0·22		0·02							2·21	2·05
O(3)						*0·66*	*0·56*	*0·72*	0·02	0·01					2·27	1·98
								0·01								
O(4)						0·01	0·36		*0·76*	*0·75*	0·18				2·26	2·06
O(5)	0·24	0·01									*0·75*	*0·74*			2·21	2·06
	0·01	0·30	0·01													
$\sum^2$	*1·00*	*1·00*	*1·00*	*1·00*	*1·00*	*1·00*	*1·00*	*1·00*	*1·00*	*1·00*	*1·00*	*1·00*	7·12	7·01	$\sigma=0·05$	

Table 1 (*cont.*)

(*d*) $HClO_4.3(H_2O)$ (Almlöf, 1972)

	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	Cl	Σ^1	Σ^2
O(1)	0·01		0·16		0·01		0·16	1·66	1·98	2·00
O(2)		0·01	0·06	0·02			0·04	1·83	1·83	2·00
			0·01	0·02			0·01			
O(3)	0·01	0·01		0·02	0·01	0·05	0·02	1·81	1·81	1·94
		0·01								
O(4)	0·16		0·02		0·01		0·03	1·78	1·94	2·05
	0·05									
O(5)	*0·75*	*0·77*	0·02		0·37	0·15	0·01		2·17	2·08
						0·01				
O(6)	0·01	0·01	*0·72*	*0·63*	*0·60*	0·01	0·01		2·16	1·99
O(7)	0·01	0·19	0·01	0·31		*0·78*	*0·72*		2·19	2·02
Σ^2	*1·00*	*1·00*	*1·00*	*1·00*	*1·00*	*1·00*	*1·00*	7·08	$\sigma=0·05$	

The workers who determined the structures point out that the Cl–O bond lengths are longer for those O atoms that act as an acceptor to a hydrogen bond. To check this correlation bond valences (S) for the Cl–O bonds were calculated from the bond lengths (R) using the empirical relation $S=(R/1·622)^{-4·7}$, where the parameters were chosen to give valence sums around Cl of 7 (average Cl–O valence = 1·75) and a reasonable correlation between the bond valences and the number of hydrogen bonds formed (Brown & Shannon, 1973). No corrections were made for the vibrational motion of the ClO_4 tetrahedra since the thermal parameters given for several of the structures may contain large systematic errors. In all the structures the ClO_4 groups appear to undergo librations of about 5° and it was assumed that these corrections would not affect the relative bond lengths. As a check on the physical reality of the distortions in the ClO_4 tetrahedra, the O–Cl–O angles were plotted against ΔS, the deviation from the average of the sum of the valences (S_1+S_2) of the two Cl–O bonds that define the angle. This plot is shown in Fig. 1 which also shows the curve* $\theta=109·5+12·9\Delta S-3·3\Delta S^2$, where $\Delta S=S_1+S_2-2S_{\text{average}}$.

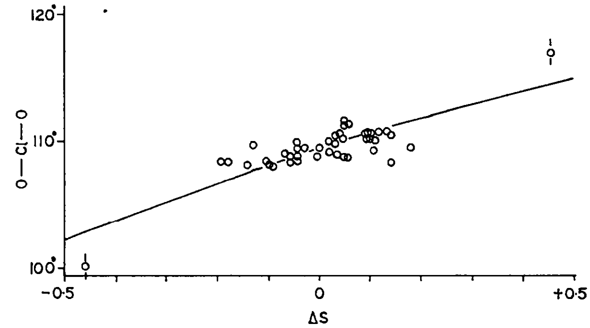

Fig. 1. Plot of O–Cl–O angle against $\Delta S=S_1+S_2-3·5$.

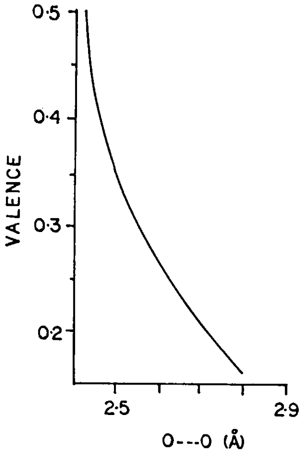

Fig. 2. Valence of H···O (acceptor) bonds *vs* O–O distance.

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* This equation is derived by assuming that a tetrahedral XO_4 group changes continuously into a planar XO_3 group by the gradual withdrawal of an O atom and that θ can be expressed as a quadratic function of ΔS. The general formula is $\theta=109·5+(90/V)\Delta S-(162/V^2)\Delta S^2$, where V is the valence of X. This prediction is close to the relationship $\theta=109·5+15·3\Delta S$ observed for sulphates (Brown, 1973). Murray-Rust, Bürgi & Dunitz (1975) have given a similar relation applicable to C_{3v} distortions of a tetrahedron.

Table 1 (*cont.*)

(*e*) $HClO_4.3\frac{1}{2}(H_2O)$ (Almlöf, 1973)

Numbering of H atoms changed from original paper.

	H(11)	H(12)	H(21)	H(22)	H(23)	H(31)	H(32)	H(41)	H(42)	H(43)	H(51)	H(52)	H(61)	H(62)	H(71)	H(72)	Cl(1)	Cl(2)	Σ^1	Σ^2
O(11)	0·01		0·01			0·03		0·02		0·01				0·02	0·04		1·80		1·80	1·94
O(12)				0·01	0·01		0·02									0·02	1·83		1·83	1·89
O(13)							0·11					0·17			0·15	0·01	1·56		1·99	2·00
O(14)					0·01							0·01	0·01	0·02		0·03	1·76		1·76	1·84
O(21)	0·01					0·03	0·07				0·01		0·03			0·14		1·75	1·89	2·04
O(22)		0·01						0·01	0·01			0·03	0·02			0·02		1·78	1·78	1·96
									0·06	0·02										
O(23)		0·05	0·02	0·02		0·02		0·01		0·01	0·01			0·02				1·76	1·76	1·92
O(24)	0·03	0·10	0·01	0·01						0·02	0·17	0·01						1·77	2·04	2·12
O(1)	*0·82*	*0·75*				0·17		0·30		0·01									2·25	2·05
O(2)			*0·58*	*0·74*	*0·67*	0·02					0·02			0·14	0·03	0·01			2·26	2·21
O(3)		0·07	0·37	0·01	0·01	*0·73*	*0·80*												2·09	1·99
O(4)	0·01	0·01						*0·64*	*0·66*	*0·65*	0·03	0·01	0·02	0·01					2·18	2·05
									0·01											
O(5)				0·21				0·01	0·25	0·01	*0·76*	*0·77*							2·12	2·01
O(6)	0·12	0·01						0·01	0·01	0·27			*0·77*	*0·79*		0·01			2·10	1·99
O(7)			0·01		0·30								0·15		*0·78*	*0·76*			2·16	2·00
Σ^2	*1·00*	*1·00*	*1·00*	*1·00*	*1·00*	*1·00*	*1·00*	*1·00*	*1·00*	*1·00*	*1·00*	*1·00*	*1·00*	*1·00*	*1·00*	*1·00*	6·95	7·06	$\sigma=0·08$	

The two extreme points in Fig. 1 are those for gaseous $HClO_4$ determined by electron diffraction (Akishin, Vilkov & Rosolovskii, 1959). Although the angular deviations are small, the general agreement between the observed and predicted angles gives further confidence that the distortions of the ClO_4 group are real.

Valences for the H–O bonds were obtained as follows: For strong bonds, those with O–O < 2·7 Å, the H···O(acceptor) valence was determined from the O–O distance using Fig. 2 which is taken from Fig. 4 of Brown (1976), modified in a way that was found to give better valence sums around the hydronium ions and water molecules. The valence for bonds with O–H distances longer than 1·7 Å was determined from Fig. 3 which is the same as Fig. 3 of Brown (1976), extrapolated in such a way as to give the best values for the valence sums around O as discussed below. Since the O(donor)–H distances were not directly measured their valences were inferred by ensuring that the valence sums around H were equal to 1·00. The geometries of all the hydrogen bonds are listed in Table 2.

Results

The valences of bonds in the perchloric acid hydrates are listed in Table 1(*a*) to (*e*). The valence sums around the O atoms are given in the last two columns, the first sums being those obtained if only O–H distances less than 2·30 Å are included, the second being those

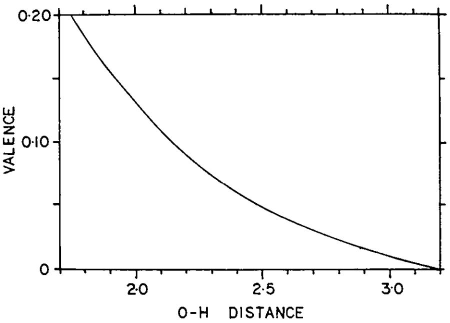

Fig. 3. Bond valence *vs* H···O (acceptor) distance.

Table 2. *Geometry of hydrogen bonds*

ClO_4^- as acceptor: left and centre columns. H_2O and H_3O^+ as acceptor: right column. Distances in Å, angles in degrees.

HYDROGEN BONDS IN H CL.O4 (H2.O)1.0

DONOR		ACCEPTOR	H...O	OHO	O...O	VALENCE
O(5)	H(3)	O(1)	2.62	121	3.224	.04
O(5)	H(1)	O(1)	2.70	98	2.943	.03
O(5)	H(3)	O(1)	2.85	86	2.943	.02
O(5)	H(2)	O(1)	2.85	87	2.943	.02
O(5)	H(1)	O(2)	1.66	169	2.651	.26
O(5)	H(2)	O(2)	3.00	57	2.651	.01
O(5)	H(2)	O(2)	2.69	119	3.251	.03
O(5)	H(3)	O(2)	2.96	98	3.251	.01
O(5)	H(2)	O(3)	1.69	173	2.704	.21
O(5)	H(1)	O(3)	3.06	56	2.704	.01
O(5)	H(2)	O(3)	2.73	162	3.056	.03
O(5)	H(1)	O(3)	2.83	103	3.159	.02
O(5)	H(3)	O(3)	2.86	97	3.159	.02
O(5)	H(3)	O(4)	1.62	179	2.622	.27
O(5)	H(1)	O(4)	3.00	54	2.622	.01
O(5)	H(2)	O(4)	3.01	56	2.622	.01
O(5)	H(1)	O(4)	2.70	109	3.115	.03
O(5)	H(2)	O(4)	2.62	97	3.115	.02

HYDROGEN BONDS IN H CL.O4 (H2.O)2.0

DONOR		ACCEPTOR	H...O	OHO	O...O	VALENCE
O(4)	H(2)	O(1)	1.86	174	2.784	.19
O(4)	H(2)	O(1)	1.86	174	2.784	.19
O(4)	H(2)	O(1)	2.60	108	3.202	.02
O(4)	H(2)	O(1)	2.60	108	3.202	.02
O(4)	H(2)	O(2)	2.86	99	3.147	.02
O(4)	H(2)	O(2)	2.86	99	3.147	.02
O(4)	H(1)	O(2)	2.96	88	3.147	.01
O(4)	H(3)	O(2)	2.92	101	3.243	.01
O(4)	H(3)	O(2)	2.92	101	3.243	.01
O(4)	H(1)	O(2)	2.96	92	3.243	.01
O(4)	H(3)	O(3)	1.84	173	2.707	.19
O(4)	H(2)	O(3)	2.61	116	3.135	.04
O(4)	H(3)	O(3)	2.79	102	3.135	.02
O(4)	H(1)	O(3)	3.04	78	3.041	.01
O(4)	H(1)	O(3)	3.04	78	3.041	.01

HYDROGEN BONDS IN H CL.O4 (H2.O)2.5

DONOR		ACCEPTOR	H...O	OHO	O...O	VALENCE
O(4)	H(42)	O(11)	2.36	141	2.952	.12
O(3)	H(31)	O(11)	2.67	98	2.998	.03
O(3)	H(33)	O(11)	3.09	76	2.998	.01
O(2)	H(22)	O(11)	2.90	86	2.936	.01
O(5)	H(52)	O(12)	1.93	163	2.876	.15
O(5)	H(52)	O(12)	2.41	117	2.976	.06
O(2)	H(22)	O(12)	3.36	93	3.210	.01
O(4)	H(41)	O(13)	1.86	161	2.812	.16
O(3)	H(33)	O(13)	2.37	119	2.868	.06
O(3)	H(32)	O(13)	2.56	100	2.868	.05
O(5)	H(51)	O(13)	2.75	106	3.234	.02
O(5)	H(52)	O(13)	2.81	108	3.234	.02
O(4)	H(41)	O(14)	2.50	131	3.241	.02
O(1)	H(13)	O(14)	2.35	107	2.982	.04
O(1)	H(11)	O(14)	2.60	102	2.982	.04
O(3)	H(31)	O(14)	2.74	99	3.073	.03
O(3)	H(32)	O(14)	2.79	96	3.073	.02
O(3)	H(33)	O(14)	2.83	95	3.073	.02
O(4)	H(42)	O(14)	2.62	98	3.065	.02
O(5)	H(51)	O(14)	2.82	99	3.159	.02
O(2)	H(21)	O(14)	2.92	63	2.967	.01
O(4)	H(42)	O(21)	2.41	118	2.971	.06
O(2)	H(21)	O(21)	2.59	110	3.136	.04
O(4)	H(42)	O(21)	2.59	104	2.967	.04
O(3)	H(31)	O(21)	2.70	106	3.147	.03
O(3)	H(32)	O(21)	2.96	91	3.147	.01
O(3)	H(32)	O(21)	3.03	92	3.229	.01
O(2)	H(21)	O(22)	1.85	177	2.819	.19
O(2)	H(22)	O(22)	2.10	148	2.967	.11
O(1)	H(11)	O(22)	2.87	103	3.249	.02
O(1)	H(13)	O(22)	3.06	93	3.295	.01
O(5)	H(52)	O(22)	3.35	96	3.299	.01
O(2)	H(22)	O(23)	2.74	108	3.169	.03
O(2)	H(21)	O(23)	3.00	91	3.169	.01
O(1)	H(12)	O(23)	2.75	102	3.118	.02
O(1)	H(13)	O(23)	2.97	90	3.118	.01
O(5)	H(52)	O(23)	2.96	91	3.153	.01
O(2)	H(22)	O(23)	3.01	81	3.052	.01
O(3)	H(33)	O(23)	3.02	105	3.330	.01
O(3)	H(33)	O(24)	1.82	154	2.751	.15
O(3)	H(31)	O(24)	2.88	73	2.751	.02
O(1)	H(11)	O(24)	2.54	120	3.160	.04
O(1)	H(13)	O(24)	2.96	92	3.160	.02
O(5)	H(51)	O(24)	2.80	95	3.062	.02
O(4)	H(41)	O(24)	2.97	107	3.396	.01

HYDROGEN BONDS IN H CL.O4 (H2.O)3.0

DONOR		ACCEPTOR	H...O	OHO	O...O	VALENCE
O(6)	H(3)	O(1)	1.92	147	2.739	.16
O(6)	H(5)	O(1)	2.39	66	2.739	.01
O(7)	H(7)	O(1)	1.90	161	2.886	.16
O(5)	H(1)	O(1)	3.01	108	3.427	.01
O(6)	H(3)	O(2)	2.38	124	3.061	.06
O(6)	H(4)	O(2)	2.76	99	3.061	.02
O(6)	H(4)	O(2)	2.85	92	3.083	.02
O(6)	H(3)	O(2)	2.90	88	3.083	.01
O(7)	H(7)	O(2)	2.58	99	2.926	.04
O(7)	H(7)	O(2)	2.93	102	3.309	.01
O(5)	H(2)	O(2)	2.98	113	3.457	.01
O(7)	H(6)	O(3)	2.45	107	2.866	.05
O(7)	H(7)	O(3)	2.73	103	3.106	.02
O(6)	H(4)	O(3)	2.80	161	3.143	.02
O(6)	H(5)	O(3)	2.97	92	3.143	.01
O(5)	H(2)	O(3)	2.92	97	3.218	.01
O(5)	H(1)	O(3)	3.00	114	3.500	.01
O(5)	H(2)	O(3)	3.30	112	3.500	.01
O(5)	H(1)	O(4)	1.92	165	2.842	.16
O(5)	H(1)	O(4)	2.51	111	2.984	.05
O(7)	H(7)	O(4)	2.74	106	3.164	.03
O(6)	H(3)	O(4)	2.80	123	3.405	.02
O(6)	H(5)	O(4)	2.98	109	3.405	.01

HYDROGEN BONDS IN H CL.O4 (H2.O)3.5

DONOR		ACCEPTOR	H...O	OHO	O...O	VALENCE
O(7)	H(71)	O(11)	2.51	138	3.376	.04
O(3)	H(31)	O(11)	2.69	113	3.255	.03
O(4)	H(41)	O(11)	2.95	102	3.193	.02
O(4)	H(43)	O(11)	2.95	96	3.193	.01
O(6)	H(62)	O(11)	2.84	103	3.201	.02
O(1)	H(11)	O(11)	2.92	86	3.015	.01
O(2)	H(21)	O(11)	3.10	85	3.119	.01
O(7)	H(72)	O(12)	2.84	105	3.210	.02
O(3)	H(32)	O(12)	2.96	114	3.370	.02
O(2)	H(23)	O(12)	2.98	101	3.296	.01
O(2)	H(22)	O(12)	2.96	102	3.296	.01
O(5)	H(52)	O(13)	1.92	162	2.827	.17
O(7)	H(71)	O(13)	1.97	155	2.868	.15
O(7)	H(72)	O(13)	2.94	76	2.868	.01
O(3)	H(32)	O(13)	2.11	143	2.922	.11
O(7)	H(72)	O(14)	2.64	122	3.248	.03
O(6)	H(62)	O(14)	2.86	94	3.072	.02
O(6)	H(61)	O(14)	2.94	89	3.072	.01
O(5)	H(52)	O(14)	2.90	111	3.353	.01
O(2)	H(23)	O(14)	2.95	106	3.325	.01
O(7)	H(72)	O(21)	1.99	148	2.840	.14
O(3)	H(32)	O(21)	2.32	120	2.919	.07
O(3)	H(31)	O(21)	2.73	92	2.919	.03
O(6)	H(61)	O(21)	2.65	132	3.355	.03
O(5)	H(51)	O(21)	3.00	117	3.535	.01
O(1)	H(11)	O(21)	3.04	89	3.163	.01
O(4)	H(42)	O(22)	2.42	120	3.000	.06
O(4)	H(43)	O(22)	2.60	93	3.000	.02
O(5)	H(52)	O(22)	2.60	108	3.107	.03
O(7)	H(72)	O(22)	2.76	110	3.205	.02
O(6)	H(61)	O(22)	2.77	116	3.302	.02
O(1)	H(12)	O(22)	2.98	107	3.386	.01
O(4)	H(41)	O(22)	3.10	86	3.161	.01
O(4)	H(42)	O(22)	3.07	87	3.161	.01
O(1)	H(12)	O(23)	2.51	119	3.094	.05
O(2)	H(21)	O(23)	2.35	85	2.933	.02
O(2)	H(22)	O(23)	2.84	86	2.933	.02
O(6)	H(62)	O(23)	2.83	100	3.144	.02
O(3)	H(31)	O(23)	2.93	83	2.983	.02
O(4)	H(43)	O(23)	3.02	96	3.256	.01
O(4)	H(41)	O(23)	3.10	92	3.258	.01
O(5)	H(51)	O(23)	3.07	105	3.429	.01
O(5)	H(51)	O(24)	1.97	156	2.762	.17
O(5)	H(52)	O(24)	3.12	65	2.762	.01
O(1)	H(12)	O(24)	2.14	133	2.883	.10
O(1)	H(11)	O(24)	2.68	93	2.883	.03
O(4)	H(43)	O(24)	2.87	92	3.062	.02
O(2)	H(22)	O(24)	2.98	110	3.419	.01
O(2)	H(21)	O(24)	3.10	108	3.622	.01

HYDROGEN BONDS IN H CL.O4 (H2.O)2.0

DONOR		ACCEPTOR	H...O	OHO	O...O	VALENCE
O(4)	H(1)	O(4)	1.21	160	2.424	.48
O(4)	H(2)	O(4)	2.94	45	2.424	.02
O(4)	H(3)	O(4)	3.39	38	2.424	.01
O(4)	H(3)	O(4)	2.79	107	3.206	.02
O(4)	H(2)	O(4)	2.99	95	3.206	.02

HYDROGEN BONDS IN H CL.O4 (H2.O)2.5

DONOR		ACCEPTOR	H...O	OHO	O...O	VALENCE
O(2)	H(22)	O(1)	2.72	123	3.352	.03
O(2)	H(21)	O(1)	3.37	99	3.352	.01
O(2)	H(22)	O(1)	2.82	65	2.565	.02
O(2)	H(21)	O(1)	3.03	53	2.565	.01
O(5)	H(52)	O(1)	3.02	53	2.555	.01
O(5)	H(51)	O(1)	3.06	51	2.555	.01
O(1)	H(13)	O(2)	1.61	165	2.565	.29
O(1)	H(11)	O(2)	3.01	55	2.565	.01
O(3)	H(31)	O(2)	1.66	166	2.677	.22
O(3)	H(33)	O(2)	2.69	68	2.677	.02
O(4)	H(41)	O(3)	2.81	61	2.492	.02
O(4)	H(42)	O(3)	2.96	52	2.492	.01
O(3)	H(33)	O(3)	3.07	80	3.050	.01
O(3)	H(32)	O(4)	1.50	164	2.492	.36
O(3)	H(31)	O(4)	2.90	51	2.492	.01
O(5)	H(51)	O(4)	1.77	171	2.762	.18
O(1)	H(12)	O(5)	1.56	168	2.555	.30
O(1)	H(11)	O(5)	2.97	56	2.555	.01
O(1)	H(13)	O(5)	3.03	53	2.555	.01
O(1)	H(11)	O(5)	1.72	149	2.634	.24
O(1)	H(12)	O(5)	2.92	64	2.634	.01

HYDROGEN BONDS IN H CL.O4 (H2.O)3.0

DONOR		ACCEPTOR	H...O	OHO	O...O	VALENCE
O(6)	H(5)	O(5)	1.54	176	2.478	.37
O(6)	H(3)	O(5)	2.60	60	2.478	.02
O(7)	H(6)	O(5)	2.15	156	2.834	.15
O(7)	H(7)	O(5)	3.06	69	2.834	.01
O(7)	H(6)	O(5)	3.05	59	2.755	.01
O(5)	H(2)	O(6)	2.96	127	3.639	.01
O(7)	H(6)	O(6)	2.96	49	2.543	.01
O(7)	H(7)	O(6)	2.99	52	2.543	.01
O(5)	H(1)	O(6)	3.03	46	2.478	.01
O(6)	H(4)	O(7)	1.54	175	2.543	.31
O(6)	H(3)	O(7)	2.96	55	2.543	.01
O(5)	H(2)	O(7)	1.77	174	2.755	.19
O(5)	H(1)	O(7)	3.00	71	2.755	.01

HYDROGEN BONDS IN H CL.O4 (H2.O)3.5

DONOR		ACCEPTOR	H...O	OHO	O...O	VALENCE
O(4)	H(41)	O(1)	1.61	176	2.554	.30
O(4)	H(43)	O(1)	3.07	49	2.554	.01
O(3)	H(31)	O(1)	1.87	161	2.779	.17
O(6)	H(62)	O(2)	1.96	173	2.933	.14
O(7)	H(71)	O(2)	2.71	70	2.551	.03
O(7)	H(72)	O(2)	3.10	47	2.551	.01
O(3)	H(31)	O(2)	2.80	61	2.478	.02
O(5)	H(51)	O(2)	2.86	70	2.681	.02
O(2)	H(21)	O(3)	1.54	164	2.478	.37
O(2)	H(22)	O(3)	2.96	50	2.478	.01
O(2)	H(23)	O(3)	2.98	50	2.478	.01
O(1)	H(12)	O(3)	2.30	137	3.072	.07
O(5)	H(51)	O(4)	2.97	122	3.270	.03
O(6)	H(61)	O(4)	2.69	62	2.593	.02
O(6)	H(62)	O(4)	3.00	56	2.593	.01
O(1)	H(11)	O(4)	2.94	58	2.554	.01
O(1)	H(12)	O(4)	3.07	49	2.554	.01
O(4)	H(42)	O(4)	3.65	130	3.746	.01
O(5)	H(52)	O(4)	3.08	52	2.614	.01
O(2)	H(22)	O(5)	1.74	176	2.681	.21
O(4)	H(42)	O(5)	1.82	140	2.614	.25
O(4)	H(41)	O(5)	3.02	57	2.614	.01
O(4)	H(43)	O(5)	3.04	55	2.614	.01
O(4)	H(43)	O(6)	1.64	175	2.590	.27
O(4)	H(42)	O(6)	3.01	55	2.590	.01
O(4)	H(41)	O(6)	3.04	53	2.590	.01
O(1)	H(11)	O(6)	1.94	169	2.887	.12
O(1)	H(12)	O(6)	3.08	69	2.887	.01
O(7)	H(72)	O(6)	3.35	68	2.832	.01
O(2)	H(23)	O(7)	1.60	171	2.551	.30
O(2)	H(21)	O(7)	2.94	57	2.551	.01
O(6)	H(61)	O(7)	1.95	153	2.832	.15

including all distances out to 3·10 Å. The cut-off at 2·30 Å is chosen since it gives exactly one acceptor oxygen for each H atom. The valence sums around the perchlorate O atoms calculated using only the shorter H···O distances are 0·1 to 0·2 v.u. (valence units), less than the expected value of 2·0 while those around the water O atoms are correspondingly larger as a result of the method by which the O(donor)–H valences were assigned. Adjustment of the parameters by which the bond valences are calculated cannot by itself correct the sums as many perchlorate O atoms do not partake in this hydrogen bonding scheme. Inclusion of H···O distances in the range 2·3 to 3·1 Å leads to the valence sums in the second column which deviate by only 0·06 v.u. from 2·00. Thus it can be concluded that the very weak hydrogen bonds must be included in order to give an adequate description of the bonding in terms of bond valences.

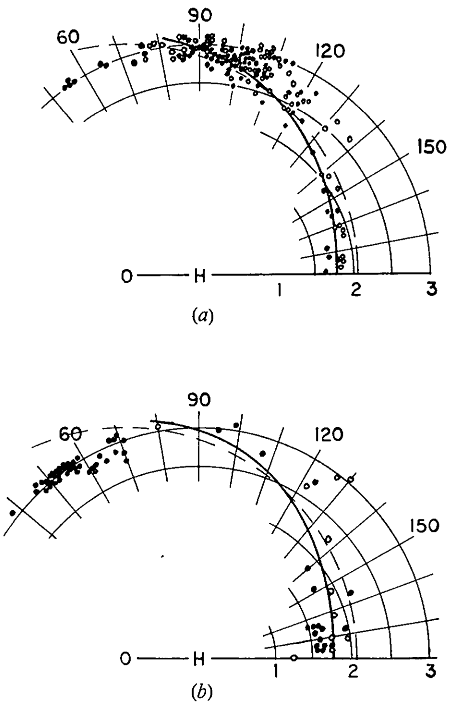

Fig. 4. Geometry of hydrogen bonds displayed on an H···O (acceptor) (Å) *vs* O–H···O angle (°) plot. (*a*) Bonds in which perchlorate groups act as acceptor, (*b*) bonds in which water molecules or hydronium ions act as acceptor. The broken line represents an O–O distance of 3 Å, the heavy line is the expected correlation (Brown, 1976). Open circles are single hydrogen bonds, filled circles are multiple hydrogen bonds.

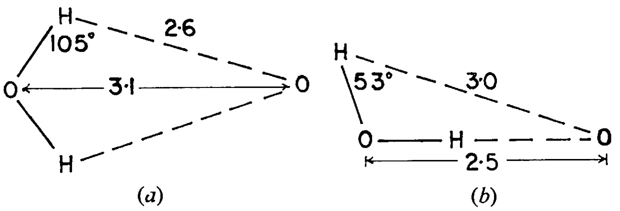

Fig. 5. Two extreme configurations for double hydrogen bonds (*a*) symmetric, (*b*) asymmetric.

Further confirmation that these distances do correspond to very weak hydrogen bonds comes from the bond geometry. Fig. 4 shows a radial plot of H···O(acceptor) distance against O–H···O angle and displays the actual geometry of each hydrogen bond in the plane of its three atoms. Fig. 4(*a*) is a composite of all the hydrogen bonds accepted by perchlorate O atoms in the five hydrates, while Fig. 4(*b*) shows the geometries of those hydrogen bonds in which the water molecules and hydronium ions are the acceptors. About twenty of the bonds to perchlorate are normal (1·6 Å < H···O < 2·2 Å; O–H···O < 130°) but the majority have O···H between 2·3 and 3·1 Å and O–H···O between 80 and 120°. Interactions in this region are often not considered hydrogen bonds (Hamilton & Ibers, 1968) but they lie along the extension of the line (the heavy line in Fig. 4) that describes the correlation between H···O distances and O–H···O angles (Brown, 1976) in the region where very weak hydrogen bonds would be expected. It is a matter of semantics whether one prefers to call them bonds or interactions, but because of their large number their influence cannot be ignored.*

A number of the bonds are multiple hydrogen bonds where two or more H atoms link the same two O atoms. These are shown by filled circles in Fig. 4. The configurations of double hydrogen bonds can vary between the two extremes of symmetric [Fig. 5(*a*)] and highly asymmetric [Fig. 5(*b*)] although in the latter case the weaker H···O distance will only be less than 3 Å if the second H···O distance is particularly short (~1·6 Å). It is significant that almost all the highly asymmetric double or triple bonds occur with water or the hydronium ion as acceptor [Fig. 4(*b*)]. Such multiple 'bonds' are a necessary result of the formation of strong hydrogen bonds and may not correspond to bonding interactions. Significantly, inclusion or exclusion of these bond valences makes little difference to the valence sums. Symmetric triple bonds are formed in both the monohydrate and the $2\frac{1}{2}$ hydrate. In each case a perchlorate O atom lies symmetrically below the three H atoms of an H_3O^+ ion and in each case the total valence contributed to the perchlorate O atom is 0·07 v.u.

Discussion

The hydrogen bonds in the perchlorate hydrates can be classified in three groups according to their strength. The H_3O^+ or $H_5O_2^+$ groups generally form strong linear hydrogen bonds with H···O acceptor bonds of between 0·2 and 0·5 v.u. and O–O distances shorter than 2·7 Å. Occasionally they also form weaker

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* The term 'bond' is used in this paper since the interactions contribute to the bonding in the crystal and do not differ in kind from stronger hydrogen bonds.

(normal) hydrogen bonds particularly when they are bonded to a perchlorate O atom. All the other water molecules act as donors to two normal hydrogen bonds with H···O(acceptor) valences lying between 0·1 and 0·2 v.u. corresponding to O–O distances in the range between 2·7 and 2·9 Å. In addition to these strong and normal hydrogen bonds, each H atom is involved in between 2 and 7 (average 4·2) weak bonds with valences in the range 0·01 to 0·07 v.u., H···O distances from 2·3 to 3·1 Å and O–O distances ranging from 2·9 to 3·7 Å although shorter O–O distances are found when the weak bond is part of an asymmetric multiple hydrogen bond.

Fig. 6 shows the strengths of H···O (ClO_4) bonds plotted against the numbers (*n*) of water molecules of hydration per ClO_4^- ion. The perchlorate ion only forms strong bonds in the monohydrate where it has to bond directly to the H_3O^+ ion. As more water is added, the H^+ ion is shielded from the ClO_4^- ion by the water molecules so as to reduce the strength of the hydrogen bonds to the perchlorate ion. As *n* increases the average strength of the normal hydrogen bonds approaches 0·15 v.u. (broken line), a value similar to that found between the H_2O molecules. For small values of *n* the distinction between the normal–strong bonds and the weak bonds is quite marked, the weak bonds only contributing about a quarter to the total valence of the ClO_4^- ion. As *n* increases, the importance of the weak bonds increases, at $n=3\frac{1}{2}$ the weak bonds contribute about half the valence and the distinction between normal and weak bonds has almost vanished. At infinite dilution one would expect a continuum of hydrogen bond strengths ranging from 0 to 0·18 v.u., with the majority being very weak.

Summary

Perchloric acid is a strong acid, meaning that it has little affinity for bonding hydrogen ions. Consequently the H^+ ion in perchloric acid hydrates is associated with the water molecules and, wherever possible, the perchlorate ion forms hydrogen bonds weaker than those found in ice. What has not hitherto been noted is the large number of very weak interactions formed between hydrogen and the O atoms on the perchlorate groups, each H and each O atom being involved in four or five such bonds. Although individually each of these bonds is too weak for its influence to be detected, because of their number they contribute as much to the cohesion of the crystals as the normal hydrogen bonds. The weak bonds have the geometry expected for the weakest hydrogen-bonding interactions even though they lie beyond the range normally considered as a hydrogen bond and involve O atoms that are separated by more than the van der Waals distance (2·8 Å). Similar very weak bonds have also been found in $Li(H_2O)_3ClO_4$ (Sequeira *et al.*, 1975).

Although the present study only deals with the hydrogen bonding in perchloric acid hydrates, it is possible to predict that similar very weak interactions might occur in other systems. The features of the perchlorate ion that give rise to the weak bonds are its large size, allowing the packing of a large number of water molecules around each ion, and its low proton affinity, *i.e.* its low formal charge or residual valence. The tetrafluoroborate and iodide ions also have the same residual valence (1 v.u.) and are only slightly smaller in size. They might therefore be expected to show similar bonding. It is significant that not only do all these ions form very strong acids but they give rise to the same unusual IR, Raman and NMR spectra in aqueous solutions (Symons, 1975).

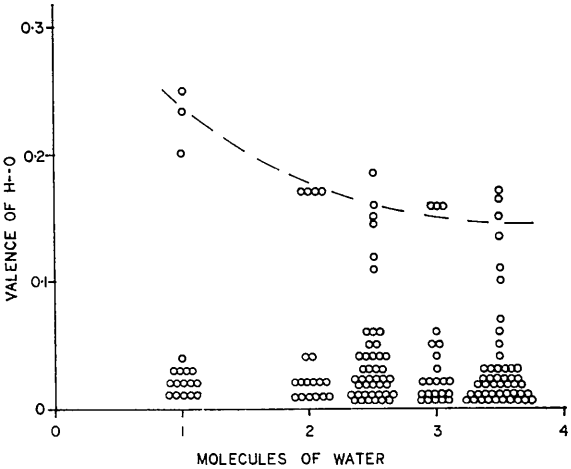

Fig. 6. Valence of H···O (perchlorate) bonds as a function of the hydration.

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