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Neutron Diffraction Study of $MgNH_4PO_4.6H_2O$ (Struvite) and Survey of Water Molecules Donating Short Hydrogen Bonds

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Abstract

$MgNH_4PO_4.6H_2O$ (struvite), $M_r = 245{\cdot}4$, $Pmn2_1$, $a = 6{\cdot}955\,(1)$, $b = 6{\cdot}142\,(1)$, $c = 11{\cdot}218\,(2)$ Å, $V = 479{\cdot}2\,(2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}70$ Mg m^{-3}, neutrons, $\lambda = 1{\cdot}179$ Å, $\mu = 0{\cdot}03$ mm^{-1}, room temperature. The structure was refined from 685 unique neutron diffraction data to $R = 0{\cdot}032$. The ammonium group is completely ordered and linked by one single and several polyfurcated N···O hydrogen bonds varying from 2·800 (5) to 3·498 (5) Å. Six out of eight W···O hydrogen bonds donated by the water molecules are in the range 2·630 (4)–2·649 (5) Å. A survey of hydrogen bonds studied by neutron diffraction reveals, on average, a linear decrease of the W···O bond length with Pauling bond strength (p) received by W from coordination bonds. From the analysis of W···O ≤ 2·66 Å it is deduced that (i) W–H *vs* W···O correlation tends to be non-linear for short W···O; (ii) short W···O's are often connected with W coordinated by M^{n+} cations with n/(coordination number) ≥ 0·5; (iii) the experimental minimum length of 2·55 Å can be explained by the hypothesis that the bond valence of W–H cannot be smaller than the bond valence received by W from coordination bonds.

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Introduction

The crystal structure of $MgNH_4PO_4.6H_2O$ (struvite) was previously reported by Whitaker & Jeffery (1970*a*) from single-crystal X-ray data. The same authors (Whitaker & Jeffery, 1970*b*) reported some evidence for an ammonium group rotating around a single hydrogen bond. Ferraris & Franchini-Angela (1973) described the structure of isomorphous arsenstruvite; they proposed a disorder restricted to two mirror positions for the ammonium group. The present neutron diffraction study was performed in order to describe the hydrogen-bonding scheme completely. An accurate determination of the configuration of the water molecules in struvite is of particular interest, because these water molecules donate some of the shortest hydrogen bonds ever found in crystalline hydrates (Chiari & Ferraris, 1982; CF, hereafter).

With the aim of understanding the correlation of morphology and structure in this phase, which is present in human calculi (Abbona & Boistelle, 1979), an X-ray refinement of the struvite structure was published (Abbona, Calleri & Ivaldi, 1984) while this research was in progress.

Table 1. *Fractional atomic coordinates and isotropic temperature factors (B equivalent) with e.s.d.'s in parentheses*

	x	y	z	B_{eq}(Å^2)
P	0	−0·0069 (6)	0·0019	1·09 (9)
Mg	0	0·3766 (6)	0·3741 (3)	1·28 (9)
O(1)	0	−0·0236 (6)	−0·1351 (3)	1·67 (9)
O(2)	0	−0·2382 (5)	0·0558 (3)	1·70 (9)
O(3)	0·1823 (3)	0·1139 (4)	0·0436 (3)	1·48 (6)
W(1)	0	0·6829 (7)	0·2878 (3)	2·66 (15)
W(2)	0	0·0768 (8)	0·4664 (4)	3·01 (15)
W(3)	0·2179 (3)	0·2618 (5)	0·2643 (3)	1·92 (9)
W(4)	0·2115 (4)	0·4852 (3)	0·4874 (3)	2·40 (9)
N	0	0·3657 (5)	0·7351 (3)	2·60 (9)
H(11)	0	0·7192 (13)	0·2017 (5)	2·81 (22)
H(12)	0	0·8174 (14)	0·3299 (6)	4·04 (32)
H(21)	0·1157 (5)	0·0070 (8)	0·4999 (4)	2·51 (24)
H(31)	0·1989 (5)	0·2007 (8)	0·1824 (4)	2·46 (14)
H(32)	0·3169 (6)	0·1702 (9)	0·3020 (4)	2·62 (14)
H(41)	0·3200 (6)	0·3904 (8)	0·5120 (4)	2·63 (14)
H(42)	0·2511 (6)	0·6354 (8)	0·5027 (4)	2·68 (14)
H(N1)	0	0·2186 (14)	0·7832 (6)	3·30 (26)
H(N2)	0	0·3311 (25)	0·6473 (7)	6·16 (53)
H(N3)	0·1148 (9)	0·4557 (13)	0·7535 (7)	5·13 (29)

Table 2. *Bond lengths* (Å) *and angles* (°) *in the phosphate tetrahedron with e.s.d.'s in parentheses*

Superscripts indicate the following equivalent positions: (i) $1/2-x$, $\bar{y}$, $1/2+z$; (ii) $\bar{x}$, y, z; (iii), $x-1/2$, $\bar{y}$, $z+1/2$; (iv) $1/2-x$, $1-y$, $1/2+z$; (v) x, $y+1$, z; (vi) x, y, $1+z$; (vii) $x-1/2$, $1-y$, $1/2+z$.

P–O(1)	1·540 (3)	O(1)–O(2)	2·515 (5)	109·2 (3)
P–O(2)	1·544 (5)	O(1)–O(3) × 2	2·518 (4)	109·6 (2)
P–O(3) × 2	1·542 (3)	O(3)–O(3) × 2	2·511 (4)	108·9 (2)
Average	1·542	O(3)–O(3^{ii})	2·536 (3)	110·7 (2)
		Average	2·518	109·5

Experimental

Crystals of struvite were grown from aqueous solution and kindly provided by F. Abbona (University of Torino). Intensities were collected from a [100] prismatic specimen 1 × 1 × 3 mm on the *P*32 automatic four-circle diffractometer at the reactor SILOE of the CENG (Grenoble). The wavelength used was $\lambda =$ 1·179 Å from a Cu (200) monochromator. About 900 reflections were registered by an $\omega/2\theta$ scan up to $\sin\theta/\lambda = 0{\cdot}66$ Å^{-1}. One test reflection was measured after every 100 reflections. The maximum variation about the mean value was about 4% of the integrated intensities during data collection. No time dependence of the intensity change could be observed.

A unique data set of 685 reflections was obtained after averaging of equivalent values; $Pnm2_1$ was confirmed. Range of h, k, l: 0–9, 0–8, 0–14. All calculations were carried out by the *XRAY*72 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The neutron scattering lengths used were from a compilation of Koester (1977): $b_P = 5{\cdot}13$, $b_{Mg} = 5{\cdot}38$, $b_O = 5{\cdot}803$, $b_N = 9{\cdot}36$, $b_H = -3{\cdot}74$ fm. The refinement (on F) was carried out with anisotropic temperature factors for all atoms. An isotropic extinction parameter was varied during the last cycles of refinement

Table 3. *Bond lengths* (Å) *and angles* (°) *in the* Mg *coordination octahedron with e.s.d.'s in parentheses*

For superscripts see Table 2.

Mg–W(1)	2·116 (6)	W(1)–W(3) × 2	3·009 (5)	91·7 (2)
Mg–W(2)	2·113 (6)	W(1)–W(4) × 2	2·941 (5)	89·7 (2)
Mg–W(3) × 2	2·076 (4)	W(2)–W(3) × 2	2·954 (5)	89·7 (2)
Mg–W(4) × 2	2·055 (4)	W(2)–W(4) × 2	2·917 (5)	88·8 (2)
Average	2·082	W(3)–W(3^{ii})	3·031 (3)	93·8 (2)
		W(3)–W(4) × 2	2·855 (5)	87·4 (2)
		W(4)–W(4^{ii})	2·942 (4)	91·4 (2)
		Average	2·943	90·0
		W(1)–W(2)		177·9 (2)
		W(3)–W(4^{ii}) × 2		178·1 (2)

and a value of $g = 0{\cdot}069 \times 10^{-3}$ was obtained. The refinement converged to final $R(F) = 0{\cdot}032$* with 149 refined parameters. Other data of the refinement are $wR = 0{\cdot}033$, $w = 1/\sigma^2(F)$, goodness of fit 0·80, $(\Delta/\sigma)_{max} = 0{\cdot}009$ for a thermal parameter of a hydrogen atom and $(\Delta/\sigma)_{av} = 0{\cdot}0016$. The unit-cell parameters reported in the *Abstract* are those published by Abbona *et al.* (1984).

Discussion

The structure

Bond lengths and angles (Tables 1, 2, 3, 4) show no major differences with respect to the values reported by Whitaker & Jeffery (1970*a*) and by Abbona *et al.* (1984). Atoms H(N2) and H(N3) show considerable thermal motion (Table 1; Fig. 1) which could suggest some kind of disorder in the ammonium group; disorder, however, was not detected, in contrast to the model of Whitaker & Jeffery (1970*b*) but in agreement with recent results of Abbona *et al.* (1984).

The hydrogen-bonding scheme of the four independent water molecules is characterized by seven bonds which are among the strongest hydrogen bonds donated by this molecule in crystalline hydrates. The eighth bond, $W(1)\cdots W(2^{v})$, however, is according to CF near to the upper limit for bonds of this type (Table 4).

The hydrogen bonds of the ammonium group are rather different, ranging from a rather short bond between H(N1) and O(1^{vi}) to a polyfurcated system of weak bonds which involve H(N2) with W(4), W(4″) and W(2) (Table 4; see Table 2 for symmetry code). Both N···O and H···O distances in this latter case are definitely within the limits given by CF and by Falk & Knop (1973) for N···O hydrogen bonds. Bond-valence arguments are required to show whether the long distances $W(1)\cdots W(2^{v})$, N···W(4)

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42684 (7pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Bond lengths* (Å) *and angles* (°) *involving the water molecules, the ammonium group and their donated hydrogen bonds with e.s.d.'s in parentheses*

D and *A* stand for donor and acceptor atoms, respectively; for superscripts see Table 2.

D–H$\cdots A$	$D\cdots A$	D–H	H–D–H	H$\cdots A$	D–H$\cdots A$	$A\cdots D\cdots A$
$W(1)$–H(11)$\cdots$O(2^{v})	2·647 (5)	0·991 (7)	106·8 (8)	1·657 (7)	176·1 (8)	119·1 (7)
–H(12)$\cdots W(2^{v})$	3·141 (5)	0·952 (9)		2·210 (7)	165·9 (8)	
$W(2)$–H(21)$\cdots$O(3^{i})	2·647 (4)	0·986 (5)	109·4 (6)	1·663 (4)	174·7 (5)	113·2 (5)
–H(21^{ii})$\cdots$O(3^{iii})	2·647 (4)	0·986 (5)		1·663 (4)	174·7 (5)	
$W(3)$–H(31)$\cdots$O(3)	2·649 (5)	1·001 (5)	105·8 (4)	1·650 (5)	175·1 (4)	105·9 (4)
–H(32)$\cdots$O(1^{i})	2·695 (4)	0·985 (5)		1·712 (5)	176·2 (5)	
$W(4)$–H(41)$\cdots$O(2^{i})	2·630 (4)	0·992 (5)	106·9 (5)	1·638 (5)	178·4 (5)	106·2 (5)
–H(42)$\cdots$O(3^{iv})	2·647 (4)	0·978 (6)		1·672 (5)	174·2 (5)	
N–H(N1)$\cdots$O(1^{vi})	2·800 (5)	1·052 (9)	108·7 (9)	1·747 (9)	179·2 (7)	
–H(N2)$\cdots W(4)$	3·229 (5)	1·008 (9)		2·505 (10)	128·3 (8)	
$\cdots W(4^{ii})$	3·229 (5)			2·505 (10)	128·3 (8)	
$\cdots W(2)$	3·498 (5)		108·7 (7)	2·561 (10)	154·6 (8)	
–H(N3)$\cdots W(3^{iv})$	3·032 (4)	0·993 (7)	111·8 (5)	2·093 (8)	157·1 (7)	
–H($N3^{ii}$)$\cdots W(3^{vii})$	3·032 (4)	0·993 (7)	107·1 (7)	2·093 (8)	157·1 (7)	

and N$\cdots W(2)$ (Table 4) are at all effective as hydrogen bonds. According to Brown's (1981) parameters, oxygen atoms $W(2)$ and $W(4)$ receive, respectively, 0·32 and 0·37 v.u. (valence units) of bond valence from Mg and transfer 0·48 and 0·49 v.u. through their donated hydrogen bonds. The deficiency in the bond valences of $W(2)$ and $W(4)$ could be accounted for by accepting that long distances $W(1)\cdots W(2^{v})$, N$\cdots W(4)$ and N$\cdots W(2)$ are effective as weak hydrogen bonds.

The large thermal motion of H(N2) and H(12) can be connected with the weakness of their hydrogen bonds (Table 4); the observed transformation of struvite into newberyite ($MgHPO_4.3H_2O$) at room temperature (Whitaker, 1968) should be kept in mind.

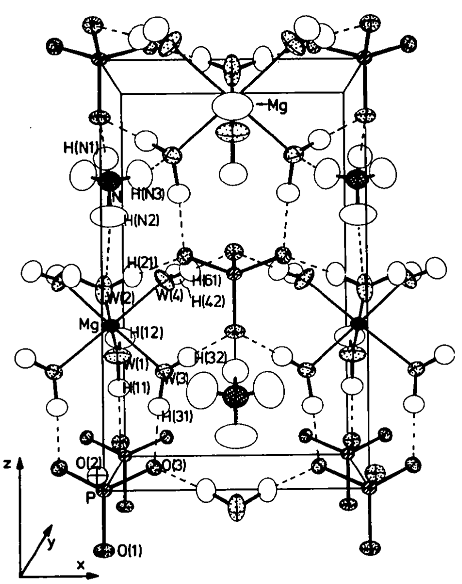

Fig. 1. Crystal structure of struvite with 50% probability thermal ellipsoids shown.

Hydrogen versus coordination bonds

Short hydrogen bonds with $W\cdots O \leq 2{\cdot}66$ Å donated by the oxygen atom of water molecules are assembled in Table 5. All of them are extracted from neutron diffraction studies of crystalline hydrates and 24 out of 40 bonds were not included in the CF paper. Table 6 lists the average $W\cdots$O and H$\cdots$O bond lengths of water molecules grouped according to Pauling's electrostatic bond strength p received from the coordination bonds [p = (charge of the cation)/(coordination number)]. Actual values and the classification scheme are taken from CF. Groups I, II, III and IV have W coordinated by cations (including H^{+}) with the total formal charges 1+, 2+, 3+ and 4+, respectively. The value of p received by W from cations is calculated on the hypothesis that they have coordination number 6 and that the bond strength received by the acceptor of a hydrogen bond is, on average, 1/6 v.u. (Baur, 1970). Since most of the hydrogen bonds of types F and K are short, the average p value was calculated from values based on individual H$\cdots W$ bond lengths and the correlation curve given by Brown (1981). In this particular case the term bond valence is usually preferred to bond strength.

The average values $(\mathrm{H}\cdots\mathrm{O})_{av}$ and $(W\cdots\mathrm{O})_{av}$ show a strong negative correlation with p (Fig. 2). These results confirm a suggestion by Falk & Knop (1973) and are analogous to findings of Ferraris & Ivaldi (1984) on protonated oxoanions. These authors report a negative correlation between the natural logarithm of p received by the donor oxygen from the central atom of the oxoanion and the $(\mathrm{O}\cdots\mathrm{O})_{av}$ of the hydrogen bonds donated by that group.

For the examples discussed in the present paper a correlation is better represented by p values than by ln p. This is probably due to the rather narrow range of values (0·24–0·67 v.u. compared with 0·75–1·67 v.u.). Bond valence (bond strength) *vs* bond length correlations (Baur, 1970; Brown & Shannon,

Table 5. *Bond lengths and angles of the hydrogen bonds donated by molecules belonging to crystalline hydrates studied by neutron diffraction and with* $W\cdots O \le 2{\cdot}66$ Å

The cations coordinating the water molecule are shown. Braces enclose values belonging to the same molecule; an x marks values not reported by Chiari & Ferraris (1982).

	Cation	$W\cdots$O (Å)	W–H (Å)	H···O (Å)	W–H···O (°)	Reference
$Al(IO_3)_3.2HIO_3.6H_2O$	Al	2·626 (5)	1·014 (7)^x	1·615 (7)	174·0 (6)	(*a*)
	Al	2·636 (4)	0·977 (5)^x	1·666 (5)	171·7 (5)	
	Al	2·596 (4)	0·985 (5)^x	1·618 (5)	171·1 (5)	
		2·641 (5)	0·992 (6)^x	1·655 (6)	172·4 (5)	
	Al	2·626 (5)	0·934 (7)^x	1·699 (7)	171·1 (7)	
	Al	2·597 (5)	1·002 (7)^x	1·598 (7)	175·1 (6)	
		2·656 (4)	0·981 (6)^x	1·688 (6)	168·4 (5)	
	Al	2·643 (5)*	0·954 (7)^x	1·693 (7)	172·8 (5)	
$Al(NO_3)_3.9D_2O$	Al	2·656 (2)	0·980 (2)^x	1·692 (2)	166·9 (2)	(*b*)
	Al	2·650 (2)	0·981 (2)^x	1·675 (2)	171·8 (2)	
		2·650 (2)	0·986 (2)^x	1·666 (2)	175·5 (2)	
$BeSO_4.4H_2O$	Be	2·617 (6)	0967 (9)	1·656 (9)	171·8 (8)	(*c*)
$CsAl(SO_4)_2.12H_2O$	Al	2·648 (7)	0·98 (2)	1·69 (2)	166 (2)	(*d*)
		2·614 (7)	0·99 (4)	1·65 (4)	164 (3)	
$Cu(HC_8O_4)_2.2H_2O$	Cu	2·658 (4)	0·973 (3)^x	1·693 (3)	170·5 (3)	(*e*)
$CuK_2(SO_4)_2.6H_2O$	Cu	2·657 (3)	0·983 (5)	1·680 (6)	171·7 (3)	(*f*)
$CuK_2(SeO_4).6H_2O$	Cu,K	2·655 (3)	0·976 (4)	1·679 (4)	178·8 (2)	(*g*)
	Cu	2·654 (3)	1·003 (4)	1·657 (4)	171·6 (2)	
$Cu_3(Zr_3F_7)_2.16H_2O$	Cu,Cu	2·602 (6)	0·997 (5)^x	1·614 (4)	170·4 (1)	(*h*)
$Fe_3(PO_4)_2.4H_2O$	Fe,Fe	2·644 (7)	1·01 (2)	1·63 (2)	176·5 (6)	(*i*)
	Fe,Fe	2·546 (5)	1·029 (10)	1·520 (9)	173·7 (9)	
$MgNH_4PO_4.6H_2O$	Mg	2·647 (5)	0·991 (7)^x	1·657 (7)	176·1 (8)	(*j*)
	H,Mg	2·647 (4)	0·986 (5)^x	1·663 (4)	174·7 (5)	
		2·647 (4)	0·986 (5)^x	1·663 (4)	174·7 (5)	
	H,Mg	2·649 (5)	1·001 (5)^x	1·650 (5)	175·1 (4)	
	H,Mg	2·630 (4)	0·992 (5)^x	1·638 (5)	178·4 (5)	
		2·647 (4)	0·978 (6)^x	1·672 (5)	174·2 (5)	
$NaAl(SO_4)_2.12H_2O$	Al	2·648 (3)	0·98 (2)	1·67 (2)	178 (2)	(*k*)
		2·623 (3)	0·99 (2)	1·64 (2)	174 (2)	
$Na_2H_2SiO_4.5H_2O$	H,Na	2·654 (8)	1·007 (13)	1·650 (13)	175 (1)	(*l*)
	Na,Na,H	2·631 (8)	0·940 (13)^x	1·692 (13)	179 (1)	
$(NH_3CH_3)Al(SO_4)_2.12H_2O$	Al	2·654 (8)	1·029 (12)^x	1·620 (3)	174·3 (1)	(*m*)
$(NH_4)Al(SO_4)_2.12H_2O$	Al	2·616 (6)	0·989 (9)^x	1·628 (2)	176·4 (1)	(*m*)
		2·593 (2)	0·960 (4)^x	1·640 (2)	171·1 (6)	
$NiK_2(SO_4)_2.6H_2O$	Ni,K	2·658 (3)	0·974 (4)	1·684 (4)	178·2 (2)	(*n*)
	Ni	2·656 (3)	0·985 (4)	1·681 (4)	170·1 (2)	
β-$Ni(IO_3)_2.2D_2O$	Ni	2·65 (2)	0·97 (2)	1·69 (2)	170 (1)	(*o*)
$UO_2(NH_2O)_2.3H_2O$	H,U	2·655 (10)	0·99 (3)	1·67 (2)	175 (2)	(*p*)
$ZnK_2(SO_4)_2.6H_2O$	Zn	2·642 (7)	0·967 (10)	1·684 (10)	170·6 (5)	(*q*)
Glycyl-L-threonine.$2H_2O$	H,H	2·650 (12)	0·946 (18)^x	1·711 (18)	174·6 (10)	(*r*)

References: (*a*) Küppers, Schäfer & Will (1982); (*b*) Hermansson (1983); (*c*) Sikka & Chidambaram (1969); (*d*) Cromer, Kay & Larson (1966); (*e*) Bartl & Küppers (1980); (*f*) Robinson & Kennard (1972); (*g*) Whitnall, Kennard, Nimmo & Moore (1975); (*h*) Chernaya *et al.* (1983); (*i*) Abrahams (1966); (*j*) this work; (*k*) Cromer, Kay & Larson (1967); (*l*) Williams & Dent Glasser (1971); (*m*) Abdeen *et al.* (1981); (*n*) Hodgeson, Whitnall & Kennard (1975); (*o*) Elemans, Van Laar & Loopstra (1972); (*p*) Adrian & Van Tets (1977); (*q*) Whitnall, Kennard & Nimmo (1975); (*r*) Sequeira, Ramanadham, Rajagopal & Padmanabhan (1981).

Table 6. *Average bond lengths concerning the hydrogen bonds donated by water molecules belonging to crystalline hydrates studied by neutron diffraction and grouped according to the Pauling's bond strength* (p) *that they receive from the coordination bonds.*

For the meaning of types see text and Chiari & Ferraris (1982) from which the averaged values are taken.

Group	Type	Number of bonds	p (v.u.)	$(H\cdots O)_{av}$ (Å)	$(W\cdots O)_{av}$ (Å)
I	*F,K*	30	0·24	1·895	2·829
II	*D,J,A,E,G*	183	0·33	1·875	2·820
III	*M,N,H,H'*	71	0·50	1·810	2·770
IV	*B,H''*	12	0·67	1·730	2·702

1973; Donnay & Allmann, 1970; Ferraris & Catti, 1973; Pyatenko, 1973) explain why a greater bond valence received by W leads to a shorter donated hydrogen bond.

The values of 2·805 and 1·857 Å reported by CF for $(W\cdots O)_{av}$ and $(H\cdots O)_{av}$, respectively, correspond to a bond valence of about 0·18 v.u. transferred to the acceptor. Hydrogen bonds that are shorter than the average value should therefore only be expected for water molecules receiving more than 0·36 v.u. from coordination bonds. On average this rule is confirmed by Table 6 and Fig. 2. Individual cases are reported in Table 5 from which it can be deduced that, usually, hydrogen bonds shorter than about 2·6 Å occur in structures containing M^{n+} cations with a coordination number (CN) such that $n/\mathrm{CN} \ge 0{\cdot}5$. The specific situation must, however, be considered. Some notable examples are:

(i) A water molecule is often donor of two hydrogen bonds with entirely different strength; *e.g.* in struvite $W(1)$ is coordinated only by one Mg from which it receives 0·33 v.u. Nevertheless, it forms a short hydrogen bond because the other bond is weak.

(ii) The short hydrogen bond in $BeSO_4.4H_2O$ is due to the coordination number 4 of Be; therefore, the coordinated W receives 0·5 v.u.

(iii) The length of the coordination bonds has to be considered for distorted polyhedra. In compounds of Cu and other transition metals coordination polyhedra with short (generally 4) and longer (generally 2) distances are observed.

(iv) The water molecule can receive more than one coordination bond, including accepted hydrogen bonds.

W–H *versus W*···O *correlation*

Fig. 3 represents the correlation of W–H bonds *versus* $W\cdots$O distances from CF completed by values of recent studies for $W\cdots O \leq 2{\cdot}66$ Å (Table 5). A

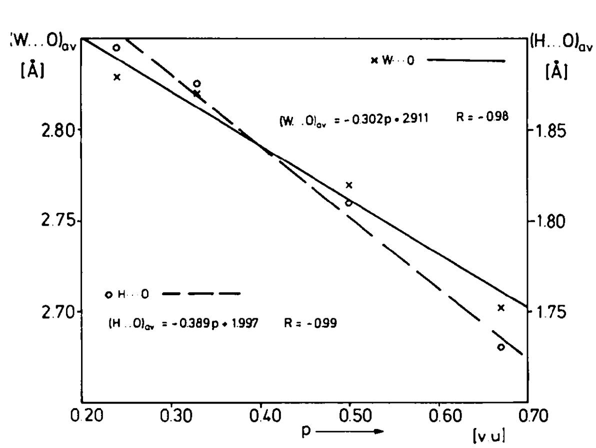

Fig. 2. Average $W\cdots$O (×) and H···O (○) bond lengths *vs* Pauling's bond strength p (v.u.) for groups of water molecules reported in Table 6. The respective regression lines for $(W\cdots O)_{av}$, full, and $(H\cdots O)_{av}$, broken, are shown.

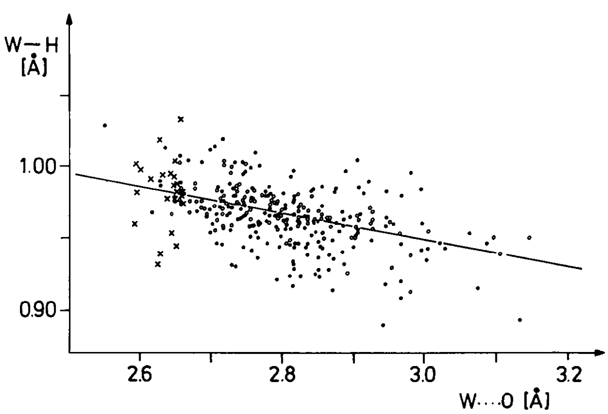

Fig. 3. Plot of W–H *vs* $W\cdots$O for water molecules belonging to crystalline hydrates studied by neutron diffraction. × correspond to the values marked x in Table 5; they are not included in the paper by Chiari & Ferraris (1982) from which the figure is taken. In that paper the legend for stars is wrong; in fact there stars and dots represent values from non-molecular structures with $\sigma \leq 0{\cdot}01$ Å and other values, respectively.

tendency of short $W\cdots$O distances to lie above the regression line is detected, despite the dispersion. The correlation curve tends to resemble the one found including any type of O···O hydrogen bond (Joswig, Fuess & Ferraris, 1982).

The shortest observed $W\cdots$O hydrogen bonds are about 2·55 Å long. This length, for a water molecule donating two equal hydrogen bonds, requires a bond valence of about 0·33 and 0·67 v.u. for each H···O and W–H bond, respectively. Consequently W must form coordination bonds with 0·67 v.u. bond valence altogether. For $W\cdots O < 2{\cdot}55$ Å, a bond valence smaller than 0·67 v.u. would be left for W–H and W should receive more than 0·67 v.u. from coordination bonds. As a matter of fact, the experimental minimum length for $W\cdots$O could be explained by the plausible hypothesis that the bond valence of W–H cannot be smaller than the bond valence received by W from coordination bonds. This limit is not observed for $(H_{2n+1}O_n)^+$ complexes which, however, constitute new entities and are therefore not discussed here.

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Structures Cristallines à 415 K (Phase II) et 295 K (Phase III) de $KFeF_4$

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Abstract

$M_r = 170{\cdot}95$, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å. Phase II: orthorhombic, *Amma* (*Cmcm*), $a = 7{\cdot}68\,(1)$, $b = 3{\cdot}92\,(1)$, $c = 12{\cdot}39\,(2)$ Å, $V = 373\,(2)$ Å^3, $Z = 4$, $D_x = 3{\cdot}043$ Mg m^{-3}, $\mu = 5{\cdot}09$ mm^{-1}, $F(000) = 324$, $T = 415\,(3)$ K, final $R = 0{\cdot}032$ for 640 reflexions. Phase III: orthorhombic, *Pmcn* (*Pnma*), $a = 7{\cdot}64\,(1)$, $b = 7{\cdot}81\,(1)$, $c = 12{\cdot}33\,(2)$ Å, $V = 735\,(3)$ Å^3, $Z = 8$, $D_x = 3{\cdot}086$ Mg m^{-3}, $\mu = 5{\cdot}17$ mm^{-1}, $F(000) = 648$, $T = 295\,(2)$ K, final $R = 0{\cdot}044$ for 1507 reflexions. The space group of III is a subgroup of II, in agreement with a phase transition involving related structures. Phase II corresponds to a $12{\cdot}4\,(2)°$ tilt along **b**, and phase III to a supplementary $6{\cdot}8\,(2)°$ tilt along **c** for FeF_6 octahedra. Corresponding notations (adapted from Glazer's notation for perovskites) are $a^0b^+c^0$ and $a^0b^+c^+$.

Introduction

Des mesures de constante diélectrique et de diffraction aux rayons X ont montré (Hidaka, Garrard & Wanklyn, 1979) que $KFeF_4$ pouvait exister, à l'état solide, sous trois formes différentes. Ainsi, par abaissement de la température, ce composé passe d'abord, à 563 K, d'une phase I (groupe *Ammm*) à une phase II (groupe *Amma*), par une transition du premier ordre qui s'accompagne du doublement du paramètre a; il existe ensuite, aux alentours de 368 K une seconde transition apparemment continue (Hidaka *et al.*, 1979), mais qui serait également du premier ordre (Saint-Grégoire, Pérez, Almairac & Lopez, 1985); cette transition se traduit par l'apparition de réflexions de surstructure, entrainant le doublement du paramètre b, et le passage à une maille de type P (phase III).

Seule a été publiée une étude structurale éffectuée à la température ambiante (Heger, Geller & Babel, 1971), dans laquelle les auteurs ont négligé les réflexions de surstructure, de faible intensité, qui différencient sur les diagrammes de diffraction X les phases II et III; la structure ainsi déterminée dans le groupe *Amma*, ne peut donc être qu'une approximation de celle de la phase II.

Il était donc nécéssaire, afin d'étudier la transition à 368 K, de connaître de façon précise les structures des phases II et III de $KFeF_4$.

Partie expérimentale

Synthèse hydrothermale à basse température (473 K) par double diffusion à partir de Fe_2O_3 et KF, dans une solution de HF.

Monocristaux de dimensions: 0,12 × 0,16 × 0,034 mm et 0,14 × 0,36 × 0,08 mm pour les études successives des phases II et III. Diffractomètre Nonius CAD-3. Phase II: cristal chauffé par jet d'air chaud.

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