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HYDROGEN BONDING IN GAIDONNAYITE*

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ABSTRACT

The two water molecules in the gaidonnayite formula donate their four hydrogen atoms to two shared and two unshared acceptor-oxygen atoms. The bond-valence sums of the three shared oxygen atoms are in excess of 2.00 v.u., indicating *d*-orbital involvement, π bonding and, as a consequence, a more ionic type of bond than is formed by the same Si with the unshared oxygen atoms.

Keywords: bond-valence sums, hydrogen bonding, shared oxygen atoms, *d* orbital, π bonding.

SOMMAIRE

Chacune des deux molécules d'eau d'hydratation de la gaidonnayite donne un atome d'hydrogène à un atome récepteur d'oxygène partagé et l'autre à un atome d'oxygène non-partagé. La somme des valences de liaison excède 2 unités de valence (v.u.) pour chacun des trois atomes d'oxygène partagés, ce qui indique l'implication des orbitales *d*, avec liaison π, et par conséquent une liaison plus ionique que celle qui unit le Si à un atome d'oxygène non-partagé.

Mots-clés: somme des valences de liaison, pont hydrogène, orbitale *d*, liaison π.

INTRODUCTION

The crystal-structure description of gaidonnayite (Chao 1985) did not dwell on the role played by the hydrogen atoms of the two water molecules in $Na_2ZrSi_3O_9 \cdot 2H_2O$. The first author therefore ran a bond-valence sum, beginning with the given atomic co-ordinates in order to check the published interatomic distances. This initial calculation showed up a misprint in the *y* co-ordinate of oxygen O(5); the given value in Table 1 of Chao (1985) is 0.1940 but should read 0.0149.

The bond-valence summation (Table 1) shows that all four hydrogen atoms are involved in hydrogen bonding. (Since all atoms in this structure are in the general 4-fold Wyckoff position of space group $P2_1nb$ and since $Z = 4$, there is one Wyckoff position associated with each atom in the formula unit.) Table 1 uses the labels of the preceding paper, except that $H_2O(1)$ and $H_2O(2)$ are now replaced by O(10) and O(11), respectively. We find that their bond-valence sums are approximately 0.4 v.u.; there is thus no doubt that the water molecules act as double donors which, as we shall see, brings their corrected bond-valence sums close to zero.

INTERPRETATION OF BOND-VALENCE SUMS AND O–O APPROACHES

The oxygen atoms of the water molecules are found to be closer than 3.15 Å to the silicate oxygen atoms O(2), O(5), O(6) and O(7). The assumed cut-off distance of 3.15 Å for hydrogen bonding is arbitrary, of course, but it is based on data collected over hundreds of well-refined structures and is the one suggested by Hamilton & Ibers (1968). The O(11) – O(2) distances of 3.140 Å, however, is so close to the cut-off value that its effect on hydrogen bonding is negligible. The $H_2O(1)$ molecule donates its hydrogen atoms to O(2) and O(5). The valence units associated with each hydrogen bond (Table 2) are based on the Lippincott–Schroeder equation (Donnay & Allmann 1970). The corresponding acceptor atoms for $H_2O(2)$, with O(11) the donor, are O(6) and O(7). Thus both water molecules donate one of their hydrogen bonds to a 'shared' oxygen atom, namely O(2) and O(6) (Table 1), an atom that is a link in the chain of silicate tetrahedra. These two acceptor atoms end up with bond-valence sums above 2.0 v.u., indicating *d*-orbital involvement and π bonding; the same is true for the third shared atom O(3), which does not receive a hydrogen bond. The inferred difference in bond types between Si–O–Si and Si–O bonds would help to explain the observed differences in bond lengths, which Chao (1985) discussed. The longer bonds with π character are more ionic, and they are the ones for which Pauling (1980) deduced a 50% ionic character; the shorter bonds involving an unshared oxygen atom would appear to be the more covalent (Stewart *et al.* 1980).

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TABLE 1. BOND LENGTHS AND VALENCE SUMS IN GAIDONNAYITE

	Si(1)	Si(2)	Si(3)	Na(1)	Na(2)	Zr	Σv_c (v.u.)	Nature of oxygen atom	H-bond corrected Σv_c (v.u.)	
O(1)	1.606(6) 1.047			3.006(6) 0.040(0)	2.545(7) 0.165(1)	2.077(5) 0.667(5)	1.920(13)		1.920(13)	(1)
O(2)	1.647(6) 0.964	1.631(5) 0.985(9)					1.949(14)	+(...H)* from H_2O(1)	2.124$^{\Psi}$(14)	(2)
O(3)	1.651(5) 0.956(9)		1.628(5) 0.989(9)	2.637(6) 0.160(1)			2.105(12)		2.105$^{\Psi}$(12)	(3)
O(4)	1.613(5) 1.033			2.527(6) 0.200(2)		2.048(5) 0.702(6)	1.934(11)		1.934(11)	(4)
O(5)		1.631(6) 0.985			2.622(6) 0.144(1)	2.071(6) 0.674(7)	1.802(13)	+(...H)* from H_2O(1)	1.927(13)	(5)
O(6)		1.623(6) 1.000	1.655(6) 0.936				1.936(15)	+(...H)* from H_2O(2)	2.101$^{\Psi}$(15)	(6)
O(7)		1.608(5) 1.031			2.575(6) 0.157(1)	2.115(5) 0.623(5)	1.810(11)	+(...H)* from H_2O(2)	1.935(11)	(7)
O(8)			1.611(5) 1.023	2.583(6) 0.178(2)		2.071(5) 0.674(5)	1.875(11)		1.875(11)	(8)
O(9)			1.597(5) 1.052		2.563(7) 0.160(1)	2.083(4) 0.660(4)	1.872(10)		1.872(10)	(9)
O(10)				2.465(8) 0.227(3)	2.462(8) 0.191(2)		0.418(3)	-(-H)† to O(2) and O(5)	0.118(3)	H_2O(10)
O(11)				2.537 0.195(4)	2.485(8) 0.183(2)		0.379(4)	-(-H)† to O(6) and O(7)	0.019(4)	H_2O(11)
L(Mean)	1.629	1.623	1.623	2.626	2.542	2.077				
L(Max)	2.130	2.130	2.130	3.130	3.130	2.650				
P(Exp)	3.254	3.203	3.199	5.208	4.323	3.629				
V(I)	4.00/4	4.00/4	4.00/4	1.00/6	1.00/6	4.00/6				
Norm.F.	0.999	1.000	0.999	0.980	0.997	1.000				
Σv_A(v.u.)	4.000	4.000	4.000	1.000	1.000	4.000				

(...H)* = H-bond acceptor

(-H)† = H-bond donor

Ψ this high sum indicates π bonding (*i.e.* d-orbital involvement) in the Si(1)-O(2) and Si(2)-O(2) bonds

TABLE 2. BOND-VALENCE TRANSFER BASED ON O-O APPROACH

Acceptor \ Donor	O(10) from H_2O(1)	O(11) from H_2O(2)	Bond-valence sum corrected for H bonds (v.u.)
O(2)	2.775Å 0.175v.u.		1.949 +0.175 2.124 ≈ 2.1
O(5)	2.919 0.125		1.802 +0.125 1.927 ≈ 1.9
O(6)		2.797 0.165	1.936 0.165 2.101 ≈ 2.1
O(7)		2.911 0.125	1.810 +0.125 1.935 ≈ 1.9
Σv for acceptor	0.300	0.290	
Σv for donor	0.418 -0.300	0.379 -0.360	
	0.118	0.019	

CONCLUSION

Hydrogen bonding to shared oxygen atoms should be looked for in other silicates. See, for example, the case of pyroxenes (Martin & Donnay 1972), where the formula need not give such clear-cut indication of possible H-bonding as in gaidonnayite. Partial substitution of OH for O may lead to some degree of hydrogen bonding. To put it another way: we should not accept the observed elongation of Si–O–Si bonds as evidence that shared oxygen atoms are satisfied with lower bond-valence sums than are unshared oxygen atoms. If shared oxygen atoms are not found to be bonded to other cations, such as O(3)–Na(1) (Table 1) in the present case, then one should look for hydrogen bonding.

The hydrogen bonding in georgechaoite (Ghose & Thakur 1985) is so similar to that in gaidonnayite that it does not deserve separate treatment.

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