– la direction de dilatation négative la plus faible correspond à la direction d'allongement de la chaîne. C'est la direction où les forces de cohésion sont les plus fortes (liaisons hydrogène).

Tableau 10. *Coefficients principaux de dilatation de l'azélamide*

T_1 à T_2	$\alpha_1 \cdot 10^6$	$\alpha_2 \cdot 10^6$	$\alpha_3 \cdot 10^6$	φ
−140 à 0 °C	254	−65	−40	47°
0 à 100 °C	950	−285	−110	55°

De l'ensemble de ces observations, il ressort que le mécanisme de la dilatation thermique de l'azélamide pourrait être le suivant:

– sous l'action d'une élévation de la température, l'agitation thermique de la molécule augmente, ce qui provoque un affaiblissement des forces de dispersion. On constate alors que la distance séparant deux molécules voisines augmente et ceci se traduit pour le cristal par une dilatation α_1 forte et positive;

– par suite de l'écartement des molécules parallèles provoqué par les chocs moléculaires, l'angle du groupement amidique avec le plan de la chaîne augmente par l'effet des liaisons NH···O faiblement élastiques. Le résultat de cette rotation est qu'il se produit un réarrangement moléculaire qui, à l'échelon du cristal se traduit par une contraction α_2 du type contraction de Poisson dans la direction de l'axe binaire;

– pour la dilatation α_3 faible et négative, l'explication n'est pas tout à fait aussi simple. Elle résulte à la fois du raccourcissement apparent de la chaîne carbonée elle-même et du déplacement des molécules mises bout à bout: en effet, en s'écartant du plan moyen commun, ces molécules sont ramenées l'une vers l'autre par la faible élasticité des liaisons hydrogène.

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The Crystal Chemistry of Zirconium Sulphates. VIII. The Structure of $Na_2[Zr(SO_4)_3].3H_2O$

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The structure of $Na_2[Zr(SO_4)_3].3H_2O$ has been determined by single-crystal X-ray analysis and refined by least-squares. The crystals, which are orthorhombic with space group $P2_12_12_1$, have the unit-cell dimensions $a=22{\cdot}16$, $b=7{\cdot}73$, $c=7{\cdot}08$ Å. The structure consists of spirals of composition $[Zr(SO_4)_3(H_2O)_2]_n$ extending in the [001] direction which are held together by the sodium atoms and a single lattice water molecule. Two of the sulphate groups form bridges between the zirconium atoms while two more sulphate groups are each doubly bonded to each zirconium atom. All sulphate groups have two terminal oxygen atoms. There are two water molecules coordinated to each zirconium atom. The hydrogen atoms of these water molecules bridge to oxygen atoms of sulphate groups and probably give rigidity to the spiral structure.

Introduction

Structural relationships between the hepta-, α- and β-pentahydrates, tetra-, γ- and α-monohydrates of $Zr(SO)_4)_2$ and of α-$Zr(SO_4)_2$ have previously been summarized, and the transformations among them discussed (Bear & Mumme, 1970). A striking feature of all of these structures was that they contained the same general arrangement of zirconium and sulphur atoms in their three-dimensional arrays. This arrangement persisted even though the hepta-, and α- and β-pentahydrates contained isolated dimeric units, the tetra-, and γ- and α-monohydrates were hydrogen-bonded layer type structures and α-$Zr(SO_4)_2$ contained a three-dimensional network.

Large ions such as the alkali or alkaline earths if introduced into such structures could be expected to occupy holes similar, for example, to those occupied by lattice water molecules in $Zr(SO_4)_2.7H_2O$ and α- and β-$Zr(SO_4)_2.5H_2O$, with the general features of the hydrate structures being retained. In addition, new but related ways of polymerization of zirconium by SO_4 groups should result from the introduction of extra sulphate groups. Some preliminary crystallographic

data have already been published by Sokol, Antanov & Zaitsev (1967) for salts of the general formula $M_2[Zr(SO_4)_3].H_2O$ (M = K, NH_4, Rb) and they also reported the formation of a double sulphate $Na_2[Zr(SO_4)_3].H_2O$. We have prepared the salt $Na_2[Zr(SO_4)_3].3H_2O$ and in the present paper describe its structure.

Experimental

Single crystals of $Na_2[Zr(SO_4)_3].3H_2O$ were grown from an aqueous solution containing $Zr(SO_4)_2.4H_2O$ (recrystallized BDH reagent) and Na_2SO_4 (BDH Analar reagent) in a 1:1 mole ratio. The solution was slowly evaporated at room temperature and the crystalline product finally dried over P_2O_5. A portion of the sample was ground for chemical analysis, density determination and for the collection of X-ray powder data. The latter (Table 1) were obtained by slow scanning a sample using a Philips proportional-counter diffractometer with a Ni filter and Cu $K\alpha_{1,2}$ radiation. Silicon powder was used as an internal calibrant. The density of the compound determined by displacement in carbon tetrachloride was $2{\cdot}68 \pm 0{\cdot}05$ g.cm^{-3}.

Table 1. *X-ray powder diffraction data for* $Na_2[Zr(SO_4)_3].3H_2O$ *with intensities evaluated by area comparison between peaks of the diffractogram*

$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	*hkl*	*I/I*
0·0048	0·0048	200	23
0·0112	0·0111	110	15
	0·0109	300	
0·0148	0·0148	210	100
0·0167	0·0167	201	13
0·0193	0·0193	400	44
0·0218	0·0218	011	37
0·0229	0·0230	111	100
	0·0227	301	
0·0326	0·0327	311	30
0·0398	0·0397	020	11
	0·0402	510	
0·0410	0·0410	120	13
	0·0402	411	
0·0434	0·0435	600	75
0·0472	0·0474	002	15
0·0508	0·0506	320	23
0·0519	0·0516	021	63
	0·0522	202	
	0·0520	511	
0·0528	0·0528	121	47
0·0553	0·0554	601	27
0·0563	0·0564	221	47
0·0576	0·0573	012	17
0·0620	0·0621	212	37
	0·0625	321	
0·0692	0·0692	710	37
0·0709	0·0709	421	19
	0·0711	701	
0·0772	0·0776	502	37
	0·0774	800	
0·0818	0·0818	521	10
0·0835	0·0833	620	13
0·0873	0·0871	022	19
	0·0875	512	
	0·0873	810	

Table 1 (*cont.*)

$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	*hkl*	*I/I*
0·0906	0·0906	130	24
	0·0909	602	
0·0950	0·0951	621	10
0·0989	0·0990	720	17
	0·0991	811	
0·1012	0·1013	031	14
	0·1008	612	
0·1105	0·1108	721	36
0·1162	0·1165	013	5
	0·1165	712	
0·1176	0·1177	113	16
	0·1174	303	
	0·1173	522	
0·1202	0·1206	431	32
	0·1197	911	
0·1371	0·1368	032	29
	0·1368	503	
0·1421	0·1416	223	17
0·1463	0·1463	023	22
	0·1467	513	
	0·1463	722	
	0·1463	11,00	
0·1851	0·1850	922	12
0·2038	0·2042	214	21
	0·2035	11,12	
	0·2043	13,00	

Integrated Weissenberg data for the levels *h0l* and *hk*0 up to *hk*5 were collected with Cu $K\alpha$ radiation and multiple-film packs from a crystal measuring $0{\cdot}02 \times 0{\cdot}02 \times 0{\cdot}1$ mm. Intensities were measured visually by comparison with a calibrated scale.

Subsequent data handling including interlayer scaling procedures and scattering curves for Zr, S and O were as discussed in part I (Bear & Mumme, 1969*a*). The scattering curve for Na was the un-ionized one taken from *International Tables for X-ray Crystallography* (1962).

The approximate unit-cell parameters obtained from the single-crystal data were used to index the powder diffraction data which were subsequently refined by least-squares (Table 1) to give the more precise lattice parameters listed in Table 2.

Table 2. *Crystallographic data for* $Na_2[Zr(SO_4)_3].3H_2O$

Symmetry	Orthorhombic
Unit-cell dimensions	$a = 22{\cdot}16 \pm 0{\cdot}005$ Å
	$b = 7{\cdot}73 \pm 0{\cdot}005$
	$c = 7{\cdot}08 \pm 0{\cdot}005$
Possible space group	$P2_12_12_1$
D_x	2·63 g.cm^{-3}
D_m	$2{\cdot}68 \pm 0{\cdot}05$ g.cm^{-3}
Z	4
μ_c (Cu $K\alpha$)	141 cm^{-1}

Structure determination

The *b* and *c* axis Weissenberg photographs showed that the compound was orthorhombic, and the systematic absences defined the space group as $P2_12_12_1$. From the unit-cell volume and measured density Z was calculated to be 4, as required for the above space group.

Table 3. *Comparison of observed and calculated structure factors*

h	k	l	F_o	$\|F_c\|$	h	k	l	F_o	$\|F_c\|$	h	k	l	F_o	$\|F_c\|$	h	k	l	F_o	$\|F_c\|$	h	k	l	F_o	$\|F_c\|$	h	k	l	F_o	$\|F_c\|$	h	k	l	F_o	$\|F_c\|$	h	k	l	F_o	$\|F_c\|$
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Table 4. *Fractional atomic parameters and temperature factors*

	x	*y*	*z*	*B*
Zr(1)	0·1685 (2)	0·1770 (5)	0·0891 (9)	1·18 (5) Å^2
S(1)	0·3183 (4)	0·152 (1)	0·255 (3)	1·1 (2)
S(2)	0·0449 (5)	0·184 (2)	−0·042 (3)	1·5 (2)
S(3)	0·1466 (5)	0·385 (2)	0·411 (3)	2·1 (2)
Na(1)	0·4210 (7)	0·424 (2)	0·259 (4)	1·9 (4)
Na(2)	0·0591 (9)	0·032 (3)	0·494 (4)	3·6 (5)
O(1)	−0·003 (1)	0·292 (3)	0·036 (6)	2·9 (7)
O(2)	0·028 (2)	0·077 (4)	0·783 (6)	3·0 (8)
O(3)	0·073 (1)	0·079 (4)	0·101 (7)	1·9 (7)
O(4)	0·096 (1)	0·303 (4)	0·902 (7)	1·9 (7)
O(5)	0·084 (2)	0·445 (5)	0·465 (7)	3·5 (9)
O(6)	0·148 (1)	0·189 (4)	0·392 (6)	2·0 (5)
O*W*(7)	0·218 (1)	0·355 (4)	0·883 (6)	1·4 (6)
O(8)	0·178 (1)	0·021 (4)	0·853 (6)	2·7 (7)
O(9)	0·259 (1)	0·179 (4)	0·176 (6)	1·7 (6)
O(10)	0·326 (1)	0·287 (4)	0·392 (6)	1·8 (6)
O(11)	0·362 (1)	0·159 (5)	0·097 (7)	3·0 (7)
O*W*(12)	0·329 (2)	0·093 (4)	0·715 (6)	2·8 (7)
O(13)	0·160 (2)	0·443 (4)	0·207 (6)	2·2 (7)
O*W*(14)	0·465 (1)	0·330 (4)	0·559 (6)	2·9 (5)
O(15)	0·191 (1)	0·456 (4)	0·545 (6)	2·5 (7)

Patterson functions $P(uv)$ and $P(uw)$ were used to determine a set of parameters for Zr. The positions of all other atoms except the hydrogen atoms were located by reiteration of electron density and structure factor calculation using the three-dimensional data collected about the c axis (Fig. 1).

All atom positions, together with individual isotropic temperature factors, were refined by a number of least-squares cycles, with all the data included. Refinement was halted when the shift of each variable was less than one quarter of its standard deviation. The final R was 11·4 for 850 reflexions. A comparison between F_o and F_c is given in Table 3; the atomic parameters, the temperature factors and their estimated standard deviations in Table 4, and the interatomic distances and angles in Table 5.

Table 5. *Interatomic distances and angles with e.s.d.'s in brackets*

(*a*) Within the Zr polyhedron

Zr(1)–O(6)	2·19 (2) Å
O(*W*7)	2·24 (2)
O(9)	2·09 (2)
O(13)	2·23 (2)
O(3)	2·25 (2)
O(8)	2·09 (2)
O(4)	2·25 (2)
O(*W*12)	2·29 (2)

(*b*) Within the sulphate groups

S(1) tetrahedron

S(1)–O(9)	1·45 (2) Å
O(11)	1·47 (2)
O(10)	1·44 (2)
O(8)	1·53 (3)

Angles

O(9)—S(1)–O(11)	107 (1)°
O(9)—S(1)–O(10)	106 (1)
O(9)—S(1)–O(8)	112 (1)
O(8)—S(1)–O(11)	110 (1)
O(8)—S(1)–O(10)	108 (1)
O(10)–S(1)–O(11)	114 (1)
Av.	110

Table 5 (*cont.*)

S(2) tetrahedron

S(2)–O(2)	1·47 (2) Å
O(3)	1·44 (2)
O(1)	1·46 (2)
O(4)	1·50 (2)

Angles

O(3)–S(2)–O(2)	110 (1)°
–O(1)	112 (1)
–O(4)	99 (1)
O(1)–S(2)–O(4)	107 (1)
O(2)–S(2)–O(4)	111 (1)
O(1)–S(2)–O(2)	116 (1)
Av.	109

S(3) tetrahedron

S(3)–O(6)	1·52 (3) Å
O(5)	1·51 (2)
O(15)	1·47 (2)
O(13)	1·54 (2)

Angles

O(6)—S(3)–O(5)	110 (1)°
–O(15)	114 (1)
–O(13)	102 (1)
O(5)—S(3)–O(13)	109 (1)
O(5)—S(3)–O(15)	110 (1)
O(13)–S(3)–O(15)	112 (1)
Av.	110

(*c*) The sodium coordination

Na(1) polyhedron

Na(1)–O(10)	2·54 (3) Å
O(11)	2·69 (3)
O(1)	3·15 (5)
O(2)	2·43 (3)
O(5)	2·31 (3)
O(15)	3·04 (3)
O(1)	3·44 (3)
O(4)	2·38 (3)

Na(2) polyhedron

Na(2)–O(6)	2·43 (3) Å
O(2)	2·19 (2)
O(3)	2·82 (3)
O(11)	2·41 (3)
O(1)	2·27 (3)

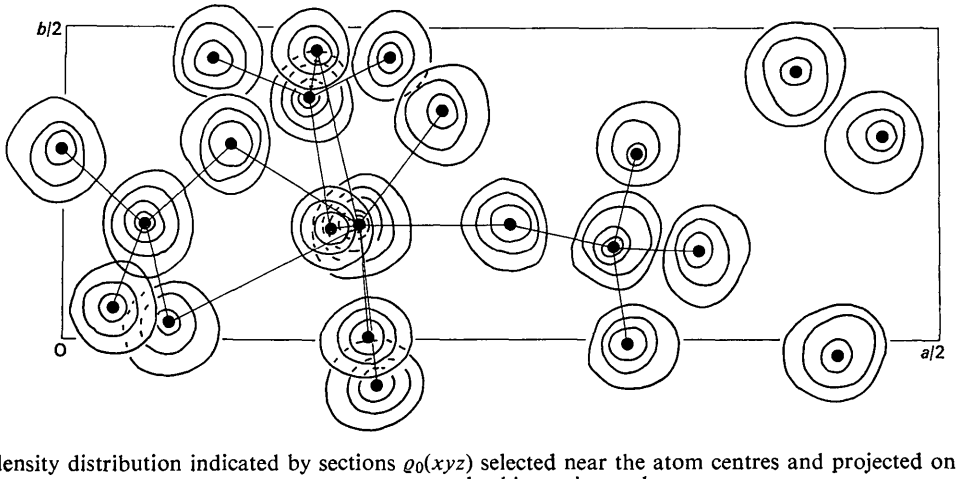


Fig. 1. Electron density distribution indicated by sections $\varrho_0(xyz)$ selected near the atom centres and projected on to (001). The contours are at equal arbitrary intervals.

Table 5 (*cont.*)

(*d*) Hydrogen bonds

Possible hydrogen bonds

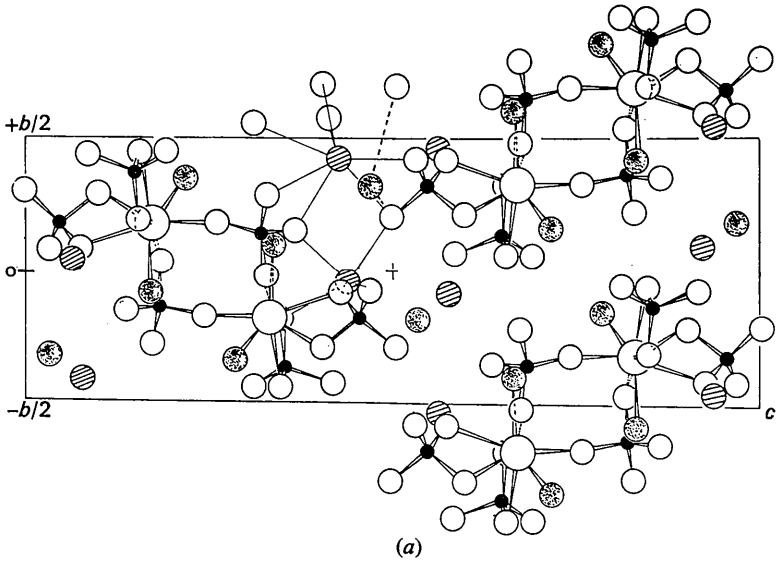
(1)	O*W*(7)	
	O(*W*7)–O(15)	2·58 (3) Å
	O(*W*7)–O(13)	2·72 (3)
	O(*W*7)–O(9)	2·63 (3)
	O(*W*7)–O(8)	2·74 (3)
Angles		
	O(15′)–O(*W*7′)–O(13)	126 (1)°
	O(9) —O(*W*7′)–O(13)	68 (1)
	O(8) —O(*W*7′)–O(13)	99 (1)
	O(15′)–O(*W*7′)–O(9)	164 (1)
	O(15′)–O(*W*7′)–O(8)	98 (1)
	O(8′)—O(*W*7′)–O(9)	72 (1)
(2)	O(*W*12)	
	O(*W*12)–O(11)	2·84 Å
	O(*W*12)–O(6)	2·56
	O(*W*12)–O(9)	2·87
	O(*W*12)–O(3)	2·67

Table 5 (*cont.*)

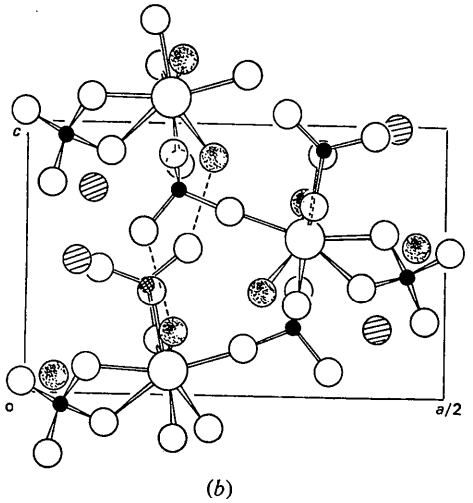
Angles		
	O(11)–O(*W*12)–O(6)	69 (1)°
	O(11)–O(*W*12)–O(9)	113 (1)
	O(11)–O(*W*12)–O(3)	100 (2)
	O(6)—O(*W*12)–O(9)	64 (1)
	O(6)—O(*W*12)–O(3)	64 (1)
	O(9)—O(*W*12)–O(3)	99 (1)
(3)	O(*W*14)	
	O(*W*14)–O(1)	
	O(*W*14)–O(1)	
Angles		
	O(1′)–O(14)–O(1)	106 (1)°

Description

The structure of $Na_2[Zr(SO_4)_3].3H_2O$ viewed in (001) and (010) projections is given in Fig. 2(*a*) and (*b*). The



(*a*)

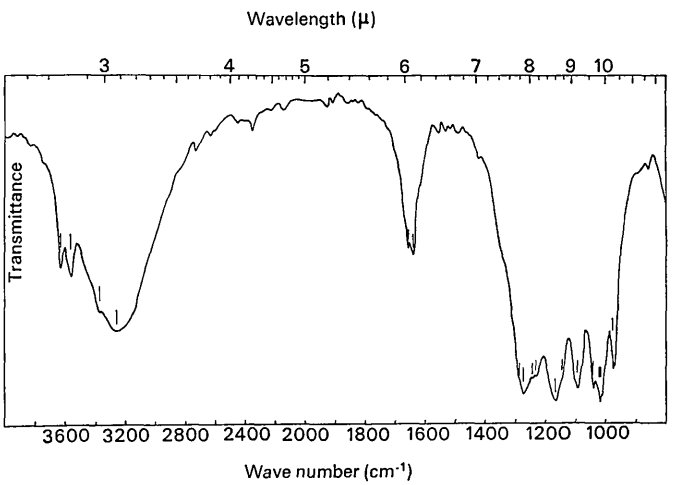


(*b*)

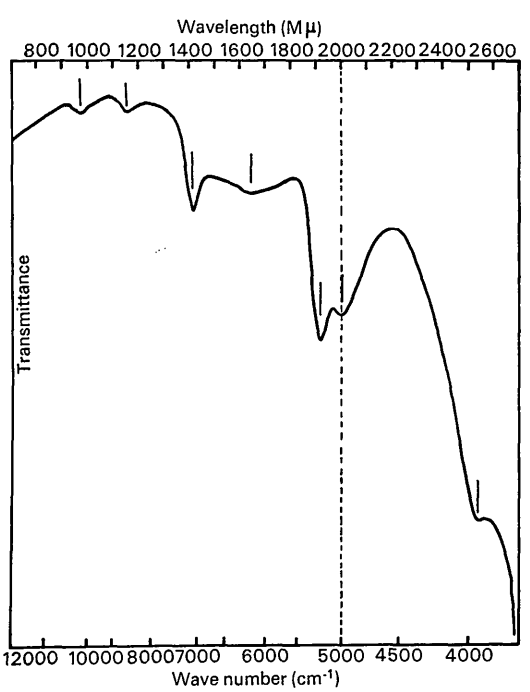
Fig. 2. The structure of $Na_2[Zr(SO_4)_3].3H_2O$ projected on to (*a*) (001), (*b*) (010). Large open circles – zirconium atoms; full circles sulphur atoms; medium open circles – oxygen atoms; stippled circles – water molecules; shaded circles – sodium atoms; hydrogen bonds – dashed lines.

main structural units which become obvious when both of these diagrams are viewed are large spirals of composition $[Zr(SO_4)_3(H_2O)_2]_n$ extending through the structure in the [001] direction. In the spirals two of the sulphate tetrahedra bridge zirconium atoms which are displaced by half unit-cell intervals in the [001] direction. These –Zr–O–S–O–Zr–O–S–O–Zr– linkages thus form a central helix. Two more doubly-bonded sulphate tetrahedra are attached to each zirconium atom of the helix. All sulphate groups have two terminal oxygen atoms and the S–O distances and O–S–O angles (Table 5) show that they are all distorted from the ideal tetrahedral symmetry. There are three non-equivalent sulphate groups in each unit cell.

The coordination of the zirconium atom is eightfold, the ligands forming a dodecahedron and each ZrO_8 polyhedron includes two coordinated water molecules. The non-bonded water molecule O*W*(14) and the two sodium ions lie between the spirals and serve to bind them together. The sodium ions, which probably contribute most to this aspect of the bonding do, however, have the additional function of bracing the large



(*a*)



(*b*)

Fig. 3. (*a*) Infrared spectrum of $Na_2[Zr(SO_4)_3].3H_2O$ recorded in Nujol and halocarbon mulls with a Beckman IR.12 grating spectrometer. (*b*) Near infrared spectrum of $Na_2[Zr(SO_4)_3].3H_2O$ recorded by diffuse reflexion from the solid samples using a Beckman DK 2A double-beam recording spectrophotometer.

Table 6. *Infrared absorption bands for* $Na_2[Zr(SO_4)_3],3H_2O$

ν_{max} (cm^{-1})	*I*	Assignments	ν_{max} (cm^{-1})	*I*	Assignments
970	*m, Shp*		3236	*S, b*	$\nu_1(H_2O)_c$
1010	*Sh*		3380	*Sh*	$\nu_3(H_2O)_c$
1015	*S*		3440	*Sh*	$2\nu_2(H_2O)$
1040	*S*		3560	*m, Shp*	$\nu_1(H_2O)_F$
1090	*S*		3630	*m, Shp*	$\nu_3(H_2O)_F$
1140	*Sh*	ν_3 and $\nu_1(SO_4)$	3937	*w*	$\nu(OH)+\nu(Zr–OW)$
1165	*S*		4975	*S*	$\nu_3(H_2O)_c+\nu_2(H_2O)$
1225	*Sh*		5236	*vs*	$\nu_3(H_2O)_F+\nu_2(H_2O)$
1240	*Sh*		6061	*W, b*	$2\nu_1(H_2O)_c$
1265	*S*		7117	*m*	$2\nu_1(H_2O)_F$
1280	*Sh*				$\nu_3+\nu_1(H_2O)_F$
1640	*m*	$\nu_2(H_2O)$	8734	*W*	$2\nu_1(H_2O)_F+\nu_2(H_2O)$
1655	*m*		10530	*W*	$3\nu_1(H_2O)_F$

$(H_2O)_c$	coordinated water molecules
$(H_2O)_F$	lattice water molecule
S	strong
m	medium
W	weak
Sh	shoulder
Shp	sharp
b	broad
vs	very strong

spiral units. To a lesser extent the hydrogen bonding of the coordinated water molecules also serves this same function. The most likely hydrogen bonds in which these two coordinated water molecules engage (Table 5, Fig. 2) are O(11)–O*W*(12)–O(3), or O(9) in one case and O(15)–O*W*(7)–O(9) or O(13) in the other. These both bridge between zirconium dodecahedra and overlying sulphate groups which are not directly bonded to these dodecahedra [see Fig. 2(*b*)].

The presence of both coordinated and lattice water molecules in this compound is clearly reflected in its infrared spectrum, shown in Fig. 3(*a*) and (*b*). Tentative assignments for the absorption bands are given in Table 6. While the three fundamental frequencies observable in the spectrum of molecular water in the vapour state are found at 3756 cm^{-1} (ν_3), 3652 cm^{-1} (ν_1) and 1595 cm^{-1} (ν_2) (Herzberg, 1954), the OH stretching frequencies ν_1 and ν_2 are lowered when the water is bound in a crystal lattice. Empirical relationships have been established between ν(OH) and O(*W*)–O distances for hydrates (Glemser & Hartat, 1955; Schubert, 1967) and in general stronger hydrogen bonds are characterized by shorter O(*W*)–O distances and lower OH stretching frequencies. In Fig. 3(*a*) and Table 5 the absorption maximum occurring near 3260 cm^{-1} can be assigned to the ν_1 stretching modes for the two coordinated water molecules, O*W*(7) and O*W*(12), both having relatively short O(*W*)–O distances (Table 5). The two sharp peaks at 3560 and 3630 cm^{-1} can be attributed to the ν_1 and ν_3 modes respectively of the single lattice water molecule, O*W*(14), which has long O(*W*)–O distances. The high frequency of these vibrations indicates that this molecule is almost completely free. It can be seen from the assignments in Table 6 that the vibrational frequencies observed in the near infrared region of the spectrum [Fig. 3(*b*)] further substantiate the presence of two types of water molecules in this compound.

As discussed in part III (Bear & Mumme, 1969*b*) the multiple absorption bands occurring in the 900–1300 cm^{-1} region of the spectrum are also in agreement with the presence of low symmetry, non-equivalent, sulphate groups in the Bravais lattice of the compound.

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