Hydrogen Bond Studies. CXVII. The Crystal Structure of $CrH(SO_4)_2 . 7H_2O$

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The crystal structure of chromium hydrogensulphate heptahydrate at 22°C has been determined from three-dimensional single-crystal X-ray data. The crystals are monoclinic, space group $P2_1/c$, with four formula units in the unit cell. The cell dimensions are: $a = 7 \cdot 3705$ (8), $b = 10 \cdot 5355$ (10), $c = 16 \cdot 7034$ (11) Å, $\beta = 109 \cdot 802$ (11)°, $V = 1220 \cdot 36$ Å^3. Six of the water molecules form an octahedron around the chromium ion. The proton of the hydrogensulphate ion has been transferred to the seventh water molecule to form an oxonium ion. The $Cr(H_2O)_6^{3+}$ and H_3O^+ ions are hydrogen bonded to sulphate ions in a three-dimensional network. The sulphate ions are the only hydrogen-bond acceptors in the structure.

Introduction

This work is the first in a series of studies of acid salts containing highly charged metal ions. Interest is centred chiefly on the formation of hydrated proton complexes and on the hydrogen-bond system. Hydrates of strong acids often contain hydrated protons, *e.g.* H_3O^+ or $H_5O_2^+$, whereas hydrates of weak acids usually crystallize as acid and water molecules, as in the case of oxalic acid dihydrate (Delaplane & Ibers, 1969) or sodium hydrogensulphate monohydrate (Grimvall, 1971). However, the structures of sulphuric acid di- and tetrahydrate contain no hydrogensulphate ions (Taesler & Olovsson, 1969; Kjällman & Olovsson, 1972). On the other hand, if a weak acid is coordinated by a highly charged metal ion, this can cause the acid to dissociate, as in the case of yttrium hydrogenoxalate trihydrate (Brunton & Johnson, 1975). It was therefore considered of interest to study other hydrates containing a moderately strong acid together with metal ions.

Experimental

Crystals of $Cr_2H_4(SO_4)_5 . 18H_2O$ were prepared according to the method described by Weinland & Krebs (1906). The crystals, together with a small amount of mother liquor, were placed on a glass plate and cooled with ice. After about two hours, crystals of $CrH(SO_4)_2 . 7H_2O$ were formed. Weinland & Krebs claim these crystals to be the octahydrate, but the present study has shown that the compound contains only seven water molecules. A prismatic crystal of dimensions $0 \cdot 280 \times 0 \cdot 093 \times 0 \cdot 053$ mm was mounted in a glass capillary, since the crystals were hygroscopic if not completely free from mother liquor. The space group was determined as $P2_1/c$ from a series of Weissenberg photographs.

The cell parameters were measured with an XDC 700 Guinier–Hägg powder camera with Cr $K\alpha_1$ radiation ($\lambda = 2 \cdot 289753$ Å) and CoP$_3$ ($a = 7 \cdot 707780$ Å) as an internal standard. A least-squares refinement with 23 observed θ values gave the cell parameters: $a = 7 \cdot 3705$ (8), $b = 10 \cdot 5355$ (10), $c = 16 \cdot 7034$ (11) Å, $\beta = 109 \cdot 802$ (11)°, $V = 1220 \cdot 36$ Å^3. The intensity data were collected at about 22°C with a PDP8/I-controlled Stoe–Philips four-circle X-ray diffractometer operating in an $\omega/2\theta$ scan mode. Mo radiation ($\lambda = 0 \cdot 71073$ Å) was used. During the data collection the crystal showed a tendency to move in its capillary. It was therefore taken out and mounted on a glass needle.

Reflexions were collected out to $\sin \theta/\lambda = 0 \cdot 65$ Å^{-1}; of the 2815 reflexions used in the final refinement, 574 were collected with the crystal in the capillary. Three standard reflexions measured periodically during the data collection showed no significant fluctuations.

The raw intensities were corrected for background and assigned standard deviations $\sigma_c(I)$ on the basis of counting statistics. The reflexions were corrected for Lorentz, polarization and absorption effects ($\mu = 6 \cdot 71$ cm^{-1}) with the program *DATAPH*. All programs used in the calculations have been described by Lundgren (1975).

Structure determination and refinement

Direct methods were used to solve the structure. Normalized structure factor amplitudes $|E|$ were calculated with the program *EFAK*. Phases were determined for reflexions with $|E| \geq 1 \cdot 5$ with the program *REL*.

The positions of the chromium ion, one of the sulphate ions and the six water oxygens were obtained from an E map. The remaining sulphate ion and the oxonium O were found from a Fourier difference synthesis following a least-squares refinement.
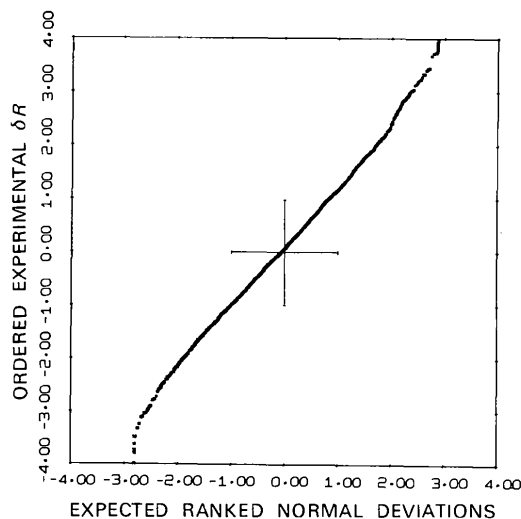
Fig. 1. A δR plot of the material after the last cycle of refinement. The slope of a least-squares line through the points is 1·13, and the y intercept is 0·09. The points for 19 reflexions are outside the plot range.

The structure was refined with the program *UPALS*. The function minimized was $\Sigma \; w(|F_o|^2 - |F_c|^2)^2$, where $w = [\sigma^2(|F_o|^2)]^{-1}$ and $\sigma^2(|F_o|^2) = \sigma_c^2(|F_o|^2) + (k|F_o|^2)^2$. The constant k was given the value 0·04. In the final cycle of refinement the 224 parameters varied were: one scale factor, one isotropic extinction parameter, the positional parameters of 33 atoms, anisotropic thermal parameters for the 18 heavy atoms and isotropic thermal parameters for the 15 H atoms.

The final agreement indices were: $R(F^2) = \Sigma \; [|F_o|^2 - |F_c|^2]/\Sigma \; |F_o|^2 = 0\cdot048$, and $R_w(F^2) = [\Sigma \; w(|F_o|^2 - |F_c|^2)^2/\Sigma \; w|F_o|^4]^{1/2} = 0\cdot083$. The conventional agreement index $R(F)$ was 0·045. A δR plot of the material is shown in Fig. 1 (Abrahams, 1974). The atomic coordinates after the last cycle are given in Table 1.* In-

Table 1. *Atomic coordinates*

Hydrogen coordinates are $\times 10^3$, others $\times 10^5$. The isotropic temperature factors for the hydrogen atoms are also given.

	x	y	z	
Cr	88411 (5)	32899 (4)	12914 (2)	
S(1)	52029 (9)	9355 (6)	29308 (4)	
S(2)	20212 (9)	32710 (6)	45131 (4)	
O(11)	56287 (29)	5029 (20)	38179 (12)	
O(12)	60086 (33)	21823 (19)	29034 (15)	
O(13)	30775 (26)	9763 (19)	24918 (12)	
O(14)	60256 (29)	−12 (20)	24786 (12)	
O(21)	12935 (29)	39631 (19)	37039 (12)	
O(22)	12571 (32)	19720 (18)	44276 (13)	
O(23)	41516 (28)	32406 (22)	47852 (14)	
O(24)	14814 (30)	39330 (19)	51758 (12)	
O(1)	87941 (33)	38426 (21)	1577 (13)	
O(2)	87525 (29)	15038 (19)	8884 (14)	
O(3)	60392 (27)	33811 (23)	9124 (14)	
O(4)	16678 (27)	31805 (21)	16663 (13)	
O(5)	90296 (28)	50657 (18)	16630 (13)	
O(6)	89108 (32)	27354 (21)	24121 (12)	
O(7)	62022 (37)	43075 (23)	39782 (15)	

	x	y	z	B (Å^2)
H(11)	786 (6)	388 (4)	14 (3)	4·1 (12)
H(12)	956 (6)	353 (4)	3 (3)	4·4 (10)
H(21)	881 (5)	87 (4)	115 (2)	3·8 (10)
H(22)	964 (7)	138 (4)	67 (3)	5·1 (11)
H(31)	540 (5)	398 (4)	97 (2)	2·6 (8)
H(32)	542 (5)	292 (4)	60 (2)	2·8 (8)
H(41)	204 (5)	259 (4)	184 (2)	2·6 (9)
H(42)	224 (5)	372 (3)	187 (2)	1·4 (7)
H(51)	849 (5)	534 (4)	197 (2)	3·5 (9)
H(52)	895 (5)	563 (4)	132 (2)	3·7 (9)
H(61)	799 (5)	260 (3)	242 (2)	2·5 (8)
H(62)	988 (6)	313 (4)	283 (2)	3·8 (9)
H(71)	533 (7)	458 (5)	354 (3)	5·9 (13)
H(72)	547 (7)	405 (5)	426 (3)	6·0 (13)
H(73)	681 (6)	482 (4)	423 (3)	3·8 (10)

Table 2. *Interatomic distances* (Å) *and angles* (°)

Cr^{3+} ion

Cr–O(1)	1·970 (2)	O(1)–Cr–O(6)	179·44 (9)
Cr–O(2)	1·992 (2)	O(2)–Cr–O(3)	91·54 (9)
Cr–O(3)	1·946 (2)	O(2)–Cr–O(4)	87·84 (9)
Cr–O(4)	1·965 (2)	O(2)–Cr–O(5)	177·11 (9)
Cr–O(5)	1·961 (2)	O(2)–Cr–O(6)	91·64 (9)
Cr–O(6)	1·945 (2)	O(3)–Cr–O(4)	179·36 (9)
		O(3)–Cr–O(5)	90·55 (9)
O(1)–Cr–O(2)	88·08 (9)	O(3)–Cr–O(6)	90·42 (10)
O(1)–Cr–O(3)	90·07 (10)	O(4)–Cr–O(5)	90·07 (9)
O(1)–Cr–O(4)	89·74 (9)	O(4)–Cr–O(6)	89·76 (9)
O(1)–Cr–O(5)	89·92 (9)	O(5)–Cr–O(6)	90·34 (9)

SO$_4^{2-}$ ion

S(1)–O(11)	1·478 (2)	O(11)–S(1)–O(14)	108·59 (12)
S(1)–O(12)	1·448 (2)	O(12)–S(1)–O(13)	109·43 (12)
S(1)–O(13)	1·488 (2)	O(12)–S(1)–O(14)	110·04 (13)
S(1)–O(14)	1·490 (2)	O(13)–S(1)–O(14)	108·07 (12)
S(2)–O(21)	1·468 (2)	O(21)–S(2)–O(22)	111·39 (12)
S(2)–O(22)	1·468 (2)	O(21)–S(2)–O(23)	108·22 (12)
S(2)–O(23)	1·480 (2)	O(21)–S(2)–O(24)	110·45 (12)
S(2)–O(24)	1·472 (2)	O(22)–S(2)–O(23)	109·99 (13)
		O(22)–S(2)–O(24)	108·80 (11)
O(11)–S(1)–O(12)	111·16 (13)	O(22)–S(2)–O(24)	107·94 (13)
O(11)–S(1)–O(13)	109·49 (11)		

Hydrogen bonds

O(1)···O(11)	2·719 (3)		
O(1)···O(22)	2·649 (3)	O(11)···O(1)···O(22)	103·54 (9)
O(2)···O(21)	2·765 (3)		
O(2)···O(24)	2·700 (3)	O(21)···O(2)···O(24)	90·5 (9)
O(3)···O(11)	2·662 (3)		
O(3)···O(23)	2·574 (3)	O(11)···O(3)···O(23)	120·98 (10)
O(4)···O(13)	2·721 (3)		
O(4)···O(14)	2·637 (3)	O(13)···O(4)···O(14)	106·25 (9)
O(5)···O(13)	2·609 (3)		
O(5)···O(22)	2·671 (3)	O(13)···O(5)···O(22)	99·69 (9)
O(6)···O(12)	2·603 (3)		
O(6)···O(21)	2·616 (3)	O(12)···O(6)···O(21)	104·16 (10)
O(7)···O(14)	2·538 (3)	O(14)···O(7)···O(23)	108·69 (11)
O(7)···O(23)	2·596 (3)	O(14)···O(7)···O(24)	114·24 (11)
O(7)···O(24)	2·591 (3)	O(23)···O(7)···O(24)	114·73 (11)
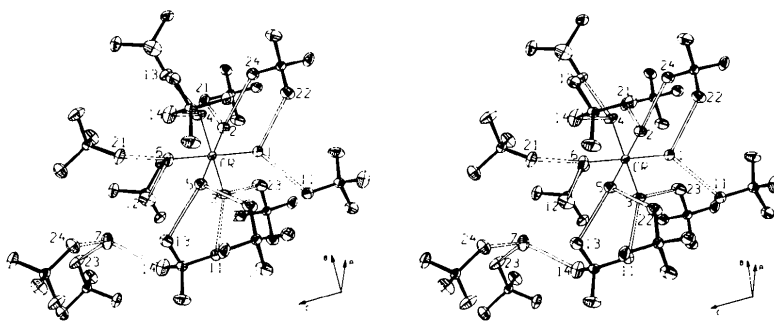
Fig. 2. A stereoscopic drawing of the crystal structure of $CrH(SO_4)_2.7H_2O$. Covalent bonds are filled, $O-H\cdots O$ bonds are open and metal—water bonds are single lines. The thermal ellipsoids are drawn to include 50% probability.

teratomic distances and angles are given in Table 2. The atomic scattering factors for Cr^{3+}, S and O were those given by Hanson, Herman, Lea & Skillman (1964). The spherical scattering factors of Stewart, Davidson & Simpson (1965) were used for H. An anomalous-dispersion correction was used for the non-hydrogen atoms (Cromer & Liberman, 1970).

Description of the structure

There is one formula unit in the asymmetric unit and all atoms are in general fourfold positions. Six water molecules form an almost regular octahedron around the chromium ion; each water molecule forms two hydrogen bonds with two sulphate ions. The seventh water molecule combines with the proton of the hydrogen-sulphate ion to form an oxonium ion which is hydrogen bonded to three sulphate ions. All sulphate oxygens except $O(12)$ accept two hydrogen bonds (Fig. 2). The three-dimensional structure is complicated. Each chromium—water octahedron is hydrogen bonded to ten sulphate ions, five involving $S(1)$ and five, $S(2)$. The sulphate ions are hydrogen bonded to five chromium—water octahedra and to one or two oxonium ions. Within the asymmetric unit there are, in all, fifteen hydrogen bonds running in a variety of directions. The hydrogen-bond system can therefore be described as constituting a three-dimensional network.

The $Cr(H_2O)_6^{3+}$ complex

The Cr—O distances to the six water oxygens are between 1·945 and 1·992 Å (Fig. 3). The O—Cr—O angles are between 87·8 and 91·6°. For chromium potassium alum, with the same octahedral arrangement, the reported Cr—O distance is 1·94 ± 0·03 Å (Bacon & Gardner, 1958). Each water molecule is hydrogen bonded to two sulphate ions. The observed apparent O—H distances in the water molecules are between 0·70 and 0·91 Å with standard deviations of roughly 0·05 Å; the H—O—H angles are between 101 and 126°. The mean value of the hydrogen-bond $O\cdots O$
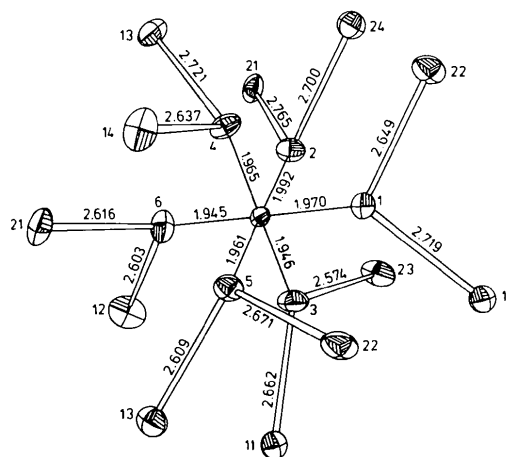

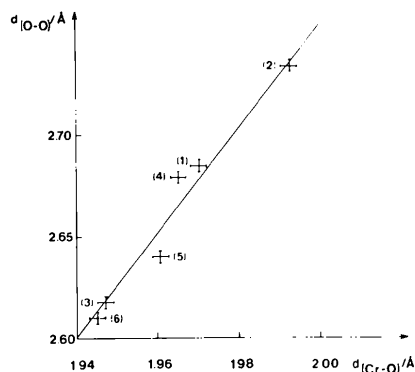Fig. 3. Bond distances (Å) in and around the chromium—water octahedron.

Fig. 4. The average of the two $O-H\cdots O$ distances vs the Cr—O distance for each water molecule. The crosses show $\pm\sigma$ for a Cr—O distance and $\pm\sigma$ for an $O-H\cdots O$ distance.

distances is 2·66 Å, in good agreement with earlier results from studies of hydrogen-bond lengths of water molecules coordinated by M^{3+} ions (Falk & Knop, 1973). In Fig. 4 the mean value of the $O\cdots O$ distances is plotted against the Cr—O distance for each water molecule. This shows a clear correlation between the Cr—O and $O\cdots O$ bond lengths.

When a water molecule has a monovalent cation or a hydrogen-bond donor as a neighbour, the coordination around the water molecule is often regular tetrahedral. Around a water molecule bonded to an M^{3+} or M^{4+} ion the coordination is usually planar trigonal (Falk & Knop, 1973). Water molecules 1 and 3 are situated in the planes defined by their hydrogen-bonded sulphate oxygens and the chromium ion. For the other water molecules there are small deviations from the planar-trigonal coordination.

The oxonium ion

The oxonium ion is hydrogen bonded to three sulphate ions, and has no contact with water molecules. The average $O \cdots O$ distance is 2·575 Å, and the average bond angle $O \cdots O \cdots O$ is 112·6° (Fig. 5). The $O-H \cdots O$ angles are all greater than 164°, and the mean apparent $O-H$ distance is 0·81 Å.
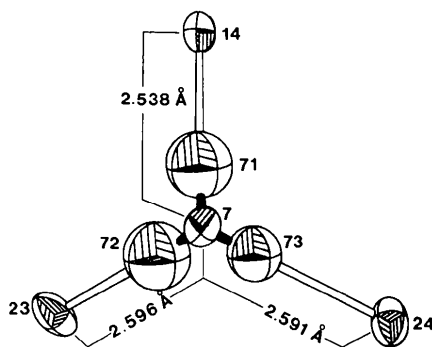

Fig. 5. The oxonium ion and its environment.

The average $O \cdots O$ distance for an oxonium ion is 2·57 Å, and the average $O \cdots O \cdots O$ bond angle is 109·3° (Lundgren & Olovsson, 1976). The environment of the oxonium ion in the present case agrees well with these results. Since the H atom positions are determined with low accuracy, the internal geometry of the oxonium ion is not discussed here.

The sulphate ions

Both sulphate ions have an almost regular tetrahedral shape, indicating that no H atom is attached to any of the sulphate O atoms (the expected S—OH distance for a hydrogensulphate ion is 1·57 Å, which is about 0·08 Å longer than the longest observed S—O bond distance). The mean S—O distance is 1·474 Å, which is in good agreement with earlier results (Taesler & Olovsson, 1969). O(12) is involved in only one hydrogen bond. It has the shortest S—O distance, 1·448 Å, as well as the largest thermal vibration. The mean O—S—O angle is, in both groups, 109·5°.

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