

Hydrogen Bond Studies.

CXXXIX.* The Structure of $\text{Cr}_4\text{H}_2(\text{SO}_4)_7 \cdot 24\text{H}_2\text{O}$

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Abstract

$\text{Cr}_4\text{H}_2(\text{SO}_4)_7 \cdot 24\text{H}_2\text{O}$ at 295 K is triclinic, $P\bar{1}$, $Z = 1$, $a = 12.6133$ (12), $b = 13.2496$ (10), $c = 7.4017$ (7) Å, $\alpha = 108.389$ (7), $\beta = 70.409$ (8), $\gamma = 112.628$ (7)°. The structure consists of oxonium ions, Cr^{3+} ions octahedrally surrounded by water molecules, and sulphate ions. In one of the two independent Cr–water octahedra, one water molecule is substituted by a sulphate O atom. The oxonium ion and the water molecules are hydrogen bonded to sulphate ions. There are no $\text{H}_2\text{O} \cdots \text{H}_2\text{O}$ or $\text{H}_3\text{O}^+ \cdots \text{H}_2\text{O}$ hydrogen bonds.

Introduction

This is the second of a series of studies of acid salt hydrates with highly charged metal ions. The high charge on the metal ion has a strong influence on the ligands. Even weak acids can dissociate when they are coordinated to such a metal ion. These salts thus often contain hydrated proton complexes of type $\text{H}(\text{H}_2\text{O})_n^+$. The water molecules can also coordinate to the metal ion. In $\text{CrH}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$ (Gustafsson, Lundgren & Olovsson, 1977), the Cr^{3+} ion is surrounded by six water molecules; only one water molecule is associated with the proton. It is therefore of interest to study compounds with different metal/proton/water ratios.

Experimental

Crystals of $\text{CrH}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$ were prepared from chromium alum, sulphuric acid and water (Weinland & Krebs, 1906). The violet crystals were heated in the presence of a small amount of mother liquor until they dissolved. The dark-green solution was kept in a beaker covered with plastic film. Small, well shaped crystals of $\text{Cr}_4\text{H}_2(\text{SO}_4)_7 \cdot 24\text{H}_2\text{O}$ formed within three to six months. Weissenberg photographs showed the crystals to be triclinic. The crystal chosen for data collection was mounted in a glass capillary. All data were

collected on an Enraf–Nonius CAD-4F κ diffractometer at 295 K with graphite-monochromatized $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073$ Å). Cell dimensions determined by least-squares refinement from the measured setting angles of 25 reflexions were $a = 12.6133$ (12), $b = 13.2496$ (10), $c = 7.4017$ (7) Å, $\alpha = 108.389$ (7), $\beta = 70.409$ (8), $\gamma = 112.628$ (7)° and $V = 1050.65$ Å³. Intensities were measured out to $\sin \theta/\lambda = 0.66$ Å⁻¹. The data were corrected for background (Lehmann & Larsen, 1974) and given e.s.d.'s based on counting statistics. Five test reflexions were measured regularly during the data collection. There was no significant change in the intensities of the two strongest test reflexions. The intensities of the three weaker test reflexions all increased. This intensity variation was well described by a linear function of time, but the lines for the three reflexions had different slopes. A small part of the low-angle data was then recollected. It was found that the intensities of most reflexions had changed, some increasing and some decreasing. No change was greater than 20% ($\sim 10\sigma$).

The whole data set was recollected with the same crystal. Four weak test reflexions were added. An analysis of the data indicated that the intensity change for each test reflexion due to crystal instability was a linear function of time. The slopes of the lines varied considerably, however. Individual corrections were applied to each reflexion on the assumption that their intensities varied linearly with time. The expected intensity at the beginning of the experiment was calculated for each reflexion from the two intensity measurements (one made in each data set). The correction formula was $I(0) = [I(t_1)t_2 - I(t_2)t_1]/(t_2 - t_1)$, where t_n is the irradiation time from the beginning of the experiment to the n th measurement of a reflexion, and $I(t)$ is the intensity of a reflexion at time t . The e.s.d.'s were modified with the function $\sigma[I(0)] = \{\sigma_c[I(t_1)]t_2 + \sigma_c[I(t_2)]t_1\}/(t_2 - t_1)$. For the test reflexions, $I(0)$ was taken from the least-squares line fitted to the measurements, and the e.s.d. used was the mean of the e.s.d.'s of all measurements of that reflexion. The reflexions were corrected for Lorentz, polarization and absorption effects ($\mu_{\text{calc}} = 1.46$ mm⁻¹). The transmission factors were 0.81–0.93.

* Part CXXXVIII: Hermansson, Thomas & Olovsson (1980).

Structure determination and refinement

The structure was determined by a combination of Patterson and direct methods. The full-matrix least-squares program *UPALS* (Lundgren, 1979) was used for the first cycles of refinement. When anisotropic thermal parameters were introduced, the large number of parameters made it necessary to use block-diagonal refinement. This was done with a modified version of *ORFLS* (Busing, Martin & Levy, 1962). Refinements were made in both $P1$ and $P\bar{1}$. No significant differences were observed between the parameters obtained in the two cases. Space group $P\bar{1}$ was thus chosen, even though this required that a sulphate group should occupy a centre of symmetry, with the O atoms disordered.

The function minimized was $\sum w(F_o^2 - F_c^2)^2$, where $w^{-1} = \sigma^2(F_c^2)$ and $\sigma^2(F_c^2) = \sigma_c^2(F_o^2) + (k|F_o^2|)^2$ with $k = 0.02$. Before the last cycle, an isotropic extinction factor was refined with *UPALS* giving $g = 0.053$ (23). The extinction- and anomalous-dispersion-corrected observed structure factor was then used as input to the last refinement cycle with the block-diagonal program.

Table 1. Atomic coordinates (for Cr, S $\times 10^5$, for O $\times 10^4$)

	x	y	z
Cr(1)	7056 (7)	84870 (6)	5533 (10)
Cr(2)	50504 (6)	71823 (6)	35655 (10)
S(1)	50000 (0)	0 (0)	0 (0)
S(2)	77322 (10)	44771 (9)	1855 (16)
S(3)	23496 (10)	29284 (9)	31892 (16)
S(4)	82138 (11)	8805 (10)	36644 (16)
O(s11)	3858 (7)	219 (9)	1224 (13)
O(s12)	5604 (8)	867 (7)	-1331 (11)
O(s13)	5690 (9)	283 (14)	1305 (18)
O(s14)	4684 (13)	8972 (7)	-1108 (15)
O(s21)	6760 (3)	4925 (2)	573 (4)
O(s22)	8773 (3)	5394 (3)	735 (4)
O(s23)	7347 (3)	3651 (3)	1375 (4)
O(s24)	1934 (3)	6022 (2)	1913 (4)
O(s31)	2304 (3)	2041 (2)	1396 (4)
O(s32)	3562 (3)	3699 (3)	3096 (5)
O(s33)	1549 (3)	3544 (2)	3389 (4)
O(s34)	1961 (3)	2403 (2)	4881 (4)
O(s41)	8800 (3)	714 (2)	1491 (4)
O(s42)	6956 (3)	677 (3)	3959 (5)
O(s43)	8412 (3)	44 (3)	4314 (4)
O(s44)	8770 (3)	2028 (3)	4625 (5)
O(1)	2223 (3)	8280 (3)	3 (7)
O(2)	9085 (4)	8533 (4)	1245 (6)
O(3)	9855 (4)	2998 (3)	1183 (5)
O(4)	5465 (3)	7778 (3)	1219 (6)
O(5)	4436 (3)	5665 (3)	2066 (5)
O(6)	1216 (4)	-49 (3)	2348 (6)
O(7)	6602 (3)	6949 (3)	2744 (5)
O(8)	167 (3)	7737 (2)	2735 (4)
O(9)	9592 (3)	5403 (3)	3480 (5)
O(10)	5332 (3)	3442 (3)	4116 (5)
O(11)	3459 (4)	7347 (4)	4331 (5)
O(12)	4346 (4)	1308 (3)	4948 (4)

This involves the refinement of one scale factor, 174 atomic coordinates and 204 anisotropic thermal parameters. The positional coordinates for the H atoms had large e.s.d.'s. Temperature factors for the H atoms were not refined, but given the value $B = 4.0 \text{ \AA}^2$. All 5134 measured reflexions were used in the refinement. The final $R_w(F^2) = \{ \sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4 \}^{1/2}$ was 0.107 and $R(F)$ was 0.167. Atomic coordinates are given in Table 1.* Scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974).

Description of the structure

There is one half formula unit in the asymmetric unit (Fig. 1). The two independent Cr^{3+} ions both coordinate six O atoms in an octahedron. One octahedron consists of water O atoms, and the other of five water O atoms and one sulphate ion. The water molecules are all hydrogen bonded to sulphate ions. One oxonium ion occurs in the structure; it is hydrogen bonded to three sulphate ions. One of the four independent sulphate groups is situated on a centre of symmetry; the O atoms were refined in half-occupied disordered positions.

The chromium–oxygen complexes and the hydrogen-bond system

The O-atom octahedra around the two Cr^{3+} ions are somewhat different. The octahedron around Cr(1) has

* Lists of structure factors, hydrogen-atom coordinates and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35141 (37 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

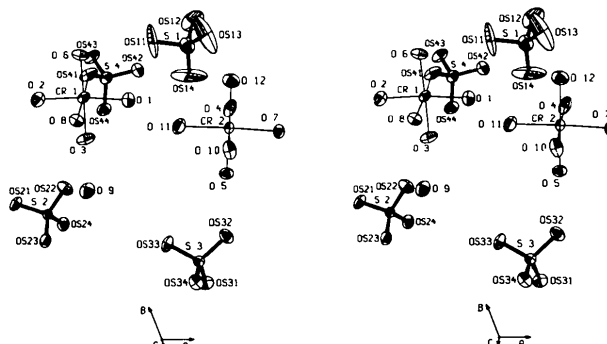


Fig. 1. A stereoscopic drawing of the asymmetric unit of $\text{Cr}_4\text{H}_2(\text{SO}_4)_7 \cdot 24\text{H}_2\text{O}$. In Figs. 1, 2, 3 and 5 covalent bonds are filled, O—H...O bonds are open and metal—oxygen bonds are single lines. Thermal ellipsoids are drawn to include 50% probability.

Cr—O distances from 1.915 to 1.991 Å (Table 2) and O—Cr—O angles from 85.6 to 93.8°. The shortest Cr—O distance is to the sulphate O atom. The distortion of the octahedron is probably caused by the sulphate ligand. The octahedron around Cr(2) is more regular, with Cr—O distances from 1.947 to 1.974 Å and O—Cr—O angles from 88.0 to 92.3°. This agrees well with the results for $\text{CrH}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$ (Gustafsson, Lundgren & Olovsson, 1977).

Eleven water molecules and one oxonium ion donate 25 hydrogen bonds, and 16 sulphate O atoms serve as hydrogen-bond acceptors (Figs. 2 and 3). Since the positions of the H atoms are poorly determined, the suggested hydrogen-bond system is based only on the positions of the non-hydrogen atoms. Most of the O atoms in sulphate groups (2), (3) and (4) accept two hydrogen bonds. There are some exceptions: O(s31) accepts three hydrogen bonds, one of which can be considered as bifurcated, with O(s41) as the other acceptor. O(s44) accepts only one ordinary hydrogen bond. One of the bonds to O(s33) can be bifurcated, with O(s44) as the other acceptor. The disordered sulphate group (1) accepts only three hydrogen bonds.

Table 2. *Interatomic distances (Å)*

Cr(1)—O(s41)	1.915 (3)	Cr(2)—O(4)	1.962 (4)
Cr(1)—O(1)	1.927 (4)	Cr(2)—O(5)	1.961 (3)
Cr(1)—O(2)	1.955 (5)	Cr(2)—O(7)	1.961 (4)
Cr(1)—O(3)	1.991 (3)	Cr(2)—O(10)	1.974 (3)
Cr(1)—O(6)	1.982 (4)	Cr(2)—O(11)	1.973 (5)
Cr(1)—O(8)	1.953 (3)	Cr(2)—O(12)	1.947 (4)
S(1)—O(s11)	1.503 (8)	S(2)—O(s21)	1.468 (3)
S(1)—O(s12)	1.551 (8)	S(2)—O(s22)	1.478 (3)
S(1)—O(s13)	1.384 (11)	S(2)—O(s23)	1.456 (3)
S(1)—O(s14)	1.335 (9)	S(2)—O(s24)	1.468 (3)
S(3)—O(s31)	1.471 (3)	S(4)—O(s41)	1.512 (3)
S(3)—O(s32)	1.469 (3)	S(4)—O(s42)	1.454 (4)
S(3)—O(s33)	1.471 (3)	S(4)—O(s43)	1.467 (3)
S(3)—O(s34)	1.473 (3)	S(4)—O(s44)	1.463 (3)
Hydrogen bonds			
O(1)···O(s11)	2.717 (10)	O(7)···O(s21)	2.700 (4)
···O(s12)	2.912 (10)	···O(s34)	2.665 (4)
···O(s13)	2.663 (13)		
···O(s14)	2.780 (15)	O(8)···O(s34)	2.646 (4)
···O(s23)	2.663 (5)	···O(s44)	2.602 (4)
O(2)···O(s31)	2.793 (5)	O(9)···O(s22)	2.654 (5)
···O(s41)	2.990 (5)	···O(s24)	2.680 (5)
···O(s43)	2.652 (5)	···O(s33)	2.580 (4)
O(3)···O(s22)	2.641 (5)	O(10)···O(s23)	2.647 (5)
···O(s33)	2.857 (5)	···O(s32)	2.747 (5)
···O(s44)	2.897 (5)		
O(4)···O(s12)	2.597 (9)	O(11)···O(s24)	2.778 (5)
···O(s31)	2.801 (5)	···O(s42)	2.693 (5)
O(5)···O(s21)	2.608 (4)	O(12)···O(s11)	2.829 (9)
···O(s32)	2.658 (4)	···O(s13)	2.896 (13)
		···O(s14)	2.658 (11)
O(6)···O(s31)	2.775 (4)	···O(s42)	2.719 (5)
···O(s43)	2.701 (5)		

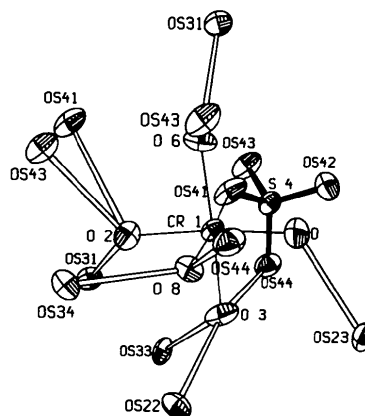


Fig. 2. The coordination and hydrogen-bond system around Cr(1).

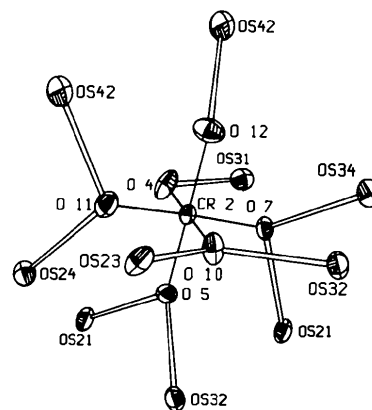


Fig. 3. The coordination and hydrogen-bond system around Cr(2).

The mean hydrogen-bond length from the water molecules is 2.70 Å (neglecting hydrogen bonds to the disordered sulphate group). This agrees well with the mean value 2.68 Å for hydrogen bonds from water molecules coordinated to M^{3+} ions (Falk & Knop, 1973). As expected, the coordination around the water molecules is almost planar. The sum of the three O···O···O and Cr—O···O bond angles is more than 345° for all water molecules where this calculation is possible. For O(2) and O(3), where one hydrogen bond can be considered as bifurcated, one of the acceptors of this bond will give a planar coordination and the other a pyramidal configuration. The mean O···O distance is plotted in Fig. 4 against Cr—O distance for each water molecule. The results for $\text{CrH}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$ are also included in the plot. The two cases agree well, but the scatter in the points from the present study is larger; points from O(2) and O(11) deviate markedly from the rest.

It is reasonable to believe that a short Cr—O distance will cause a large polarization of the water molecule, thus encouraging the formation of strong, and therefore short, hydrogen bonds.

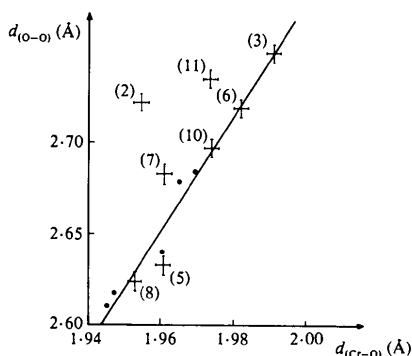


Fig. 4. The average of the two O—H...O distances vs the Cr—O distance for each water molecule. The crosses show $\pm\sigma$ for the Cr—O distance and $\pm\sigma$ for an O—H...O distance. The water molecules bonded to the disordered sulphate ion are not included. Earlier results (see text) are indicated with dots. The line is visually fitted to the material excluding points 2 and 11.

The sulphate ions

Four crystallographically different sulphate ions occur in the structure. Sulphate ions (2) and (3) are similar. They accept eight and nine hydrogen bonds from water molecules, respectively, and are almost regular tetrahedra. The mean S—O distance is 1.468 (9) Å in group (2), and 1.471 (2) Å in group (3), in agreement with a mean value of 1.473 (1) Å given by Taesler & Olovsson (1969). In sulphate group (4), O(s41) is coordinated to Cr(1). The S(4)—O(s41) distance is 1.512 (3) Å. This is significantly longer than an ordinary S—O distance but shorter than an S—OH distance in a hydrogen sulphate ion. The other S—O distances in sulphate group (4) are shortened to give a mean S—O distance, 1.474 (26) Å, near the mean values of groups (2) and (3). The three O—S—O angles not involving O(s41) are slightly opened. Sulphate group (1) is disordered; its refined geometry cannot be considered meaningful.

The H₃O⁺ ion

The oxonium ion is hydrogen bonded to three different sulphate ions in an asymmetric pyramidal bonding arrangement (Fig. 5); the O—H...O distances are

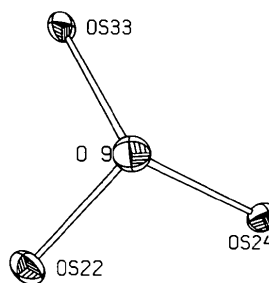


Fig. 5. The environment of the oxonium ion.

2.654 (8), 2.680 (5) and 2.580 (4) Å; O...O...O angles are 102.2 (2), 104.1 (2) and 127.0 (2)°. The average O—H...O bond distance, 2.64 Å, is slightly longer than the mean value, 2.57 Å, given by Lundgren & Olovsson (1976) for hydrogen bonds from oxonium ions. The internal geometry of the H₃O⁺ ion is not discussed here owing to the low accuracy of the H-atom parameters.

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