Support for this work was provided by grant No. GM382751 from the National Institutes of General Medical Sciences.

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Structures of Dimethylammonium Metal(III) Sulfate Hexahydrates (Metal = Al, Cr)

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(*Received* 22 *April* 1991; *accepted* 2 *August* 1991)

Abstract. (I) $[Al(H_2O)_6]^{3+}.C_2H_8N^+.2SO_4^{2-}$, $M_r = 373.28$, monoclinic, $P2_1/n$, $a = 6.408\,(1)$, $b = 10.752\,(1)$, $c = 11.134\,(2)$ Å, $\beta = 100.44\,(1)°$, $V = 754.4\,(2)$ Å^3, $Z = 2$, $D_x = 1.643$, $D_m = 1.62$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 4.7$ cm^{-1}, $F(000) = 392$, $T = 295$ K, $R = 0.040$ for 1680 reflections with $I > 4\sigma(I)$. (II) $[Cr(H_2O)_6]^{3+}.C_2H_8N^+.2SO_4^{2-}$, $M_r = 398.29$, monoclinic, $P2_1/n$, $a = 6.391\,(8)$, $b = 10.748\,(3)$, $c = 11.40\,(1)$ Å, $\beta = 100.87\,(6)°$, $V = 769\,(1)$ Å^3, $Z = 2$, $D_x = 1.720$, $D_m = 1.64$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 10.5$ cm^{-1}, $F(000) = 414$, $T = 295$ K, $R = 0.038$ for 1666 reflections with $I > 4\sigma(I)$. The Al and Cr atoms are octahedrally coordinated by the water molecules showing Al—O*w* and Cr—O*w* bond lengths ranging from 1.874 (2) to 1.891 (2) Å and from 1.953 (2) to 1.967 (2) Å, respectively. The dimethylammonium cations are disordered, with each NH_2 group having two centrosymmetric positions. The hydrogen bonds between O atoms of a sulfate anion acting as acceptors, water molecules and a dimethylammonium cation acting as a donor range from 2.586 (3) to 2.87 (1) Å.

Introduction. Trivalent metal cations (most often Al^{3+} and Cr^{3+}) form not only a variety of double sulfates with univalent alkaline and ammonium cations, but also with univalent guanidinium and substituted ammonium cations such as $(NH_3OH)^+$ and $(NH_3CH_3)^+$. Also, the corresponding alums have been studied extensively (Haussühl, 1961; Fletcher & Steeple, 1964; Ledsham & Steeple, 1969; Ledsham, Steeple & Hughes, 1970; Bol'shakova, Zalogina & Selivanova, 1971; Abdeen, Will, Schäfer, Kirfel, Bargouth, Recker & Weiss, 1981; Serezhkin, 1984; and references therein).

There are only a few reports about double sulfates of Al^{III} and Cr^{III} with dimethylammonium cations. Recently, Kirpichnikova, Andreev, Ivanov, Shuvalov & Varikash (1988) reported on the synthesis, dielectric and optical properties of dimethylammonium aluminium sulfate hexahydrate; Jordanovska (1989) reported syntheses, thermal decompositions and X-ray powder determinations of the dimethylammonium sulfate hexahydrates of Al and Cr. Continuing our work on the double salts, the crystal structure analyses of the Al and Cr salts were undertaken.

Experimental. The two title compounds were obtained as transparent colourless and violet monocrystals, respectively, by evaporation at room temperature of aqueous mixed solutions of the metal (III) sulfates and dimethylammonium sulfate in the molar ratio 1:5 (Jordanovska, 1989). Kirpichnikova *et al.* (1988) synthesized the dimethylammonium aluminium sulfate hexahydrate from a solution

0108-2701/92/020256-03\$03.00

of dimethylamine and aluminium(III) sulfate in 30% sulfuric acid and obtained transparent crystals by evaporation at 318 K. In such a way, they obtained different crystals to ours and determined preliminary unit-cell parameters of $a = 11.15$, $b = 10.74$, $c = 31.92$ Å, $\beta = 99.5°$ and point-group symmetry $2/m$.

Densities were measured pycnometrically. Intensity data collected on an Enraf–Nonius CAD-4 diffractometer using graphite-monochromatized Mo $K\alpha$ radiation; lattice parameters determined from 25 reflections with $\theta = 5$–$17°$, ω–2θ scanning technique, ω-scan width $(0.8 + 0.35\tan\theta)°$, scan rate 1.27–5.50°, the scan time extended 25% on each side for background measurements; three reference reflections [$\bar{1}\bar{1}3$, $\bar{1}13$, $0\bar{2}\bar{1}$ for (I) and $\bar{1}05$, $0\bar{3}2$, $2\bar{1}2$ for (II)] showed no significant variation in intensity. From absent reflections $h0l$, $h + l \neq 2n$ and $0k0$, $k \neq 2n$, space group $P2_1/n$ was determined for both compounds. Corrections applied for Lorentz and polarization effects, no corrections for absorption and extinction. All non-H atoms were located by Patterson and Fourier methods and water and ammonium H atoms from difference maps. The Al and Cr atoms are placed on symmetry centres. The N atoms should lie on symmetry centres, but the dimethylammonium cations cannot be centrosymmetric. It was found that the dimethylammonium cations are disordered; for this reason, the N atoms and H atoms bonded to them were included in the calculations with occupancy factors fixed at 0.5. Methyl H atoms could not be located. Full-matrix least-squares anisotropic refinements on F for the non-H atoms with fixed isotropic H atoms were employed using unit weights. Isotropic thermal parameters fixed at 0.05 and 0.09 Å^2 for the water and ammonium H atoms, respectively.

(I): Intensity data collected from a crystal of dimensions $0.21 \times 0.20 \times 0.14$ mm up to $\theta = 30°$; 2199 reflections were scanned ($0 \leq h \leq 9$, $0 \leq k \leq 15$, $-16 \leq l \leq 16$); 97 parameters were refined giving $R = 0.040$ for 1680 unique reflections with $I > 4\sigma(I)$; $(\Delta/\sigma) < 0.2$. Final difference map revealed residuals between -0.42 and 0.31 e Å^{-3} and a maximum of 0.61 e Å^{-3} close to the H(42) atom (at a distance of 0.29 Å).

(II): Intensity data collected from a crystal of dimensions $0.33 \times 0.28 \times 0.18$ mm up to $\theta = 25°$; 2204 reflections were scanned ($0 \leq h \leq 7$, $0 \leq k \leq 12$, $-13 \leq l \leq 13$); 97 parameters were refined giving $R = 0.038$ for 1666 unique reflections with $I > 4\sigma(I)$; $(\Delta/\sigma) < 0.2$. Final difference map revealed residuals between -0.60 and 0.46 e Å^{-3}.

Calculations were performed on a MicroVAX II computer using programs *SHELXS*86 (Sheldrick, 1986), *SHELX*76 (Sheldrick, 1976), *PLATON* and *PLUTON* (Spek, 1982). Scattering factors for neutral atoms from Cromer & Mann (1968).

Table 1. *Fractional positional parameters for non-*H *atoms and equivalent isotropic thermal parameters* (Å$^2 \times 10^2$)

$$U_{\rm eq} = (1/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Compound (I)				
Al†	0.0	0.5	0.5	2.13 (3)
S	0.0658 (1)	0.1828 (1)	0.2382 (1)	2.71 (2)
O(1)	0.2244 (3)	0.4339 (2)	0.4331 (2)	2.77 (5)
O(2)	0.2062 (3)	0.5754 (2)	0.6211 (2)	3.05 (5)
O(3)	0.0056 (3)	0.3536 (2)	0.5918 (2)	3.11 (6)
O(4)	0.0541 (3)	0.0470 (2)	0.2160 (2)	3.55 (6)
O(5)	0.1932 (4)	0.2057 (2)	0.3587 (2)	4.84 (7)
O(6)	−0.1502 (3)	0.2335 (2)	0.2341 (2)	3.94 (7)
O(7)	0.1612 (4)	0.2428 (2)	0.1435 (2)	4.98 (8)
N†	0.0603 (15)	0.4856 (8)	1.0445 (7)	8.2 (3)
C	0.1406 (9)	0.4744 (5)	0.9369 (5)	7.7 (2)
Compound (II)				
Cr†	0.0	0.5	0.5	2.12 (2)
S	0.0692 (1)	0.1828 (1)	0.2400 (1)	2.90 (2)
O(1)	0.2403 (3)	0.4333 (2)	0.4356 (2)	2.91 (6)
O(2)	0.2109 (4)	0.5775 (2)	0.6270 (2)	3.62 (7)
O(3)	0.0066 (3)	0.3452 (2)	0.5904 (2)	3.51 (7)
O(4)	0.0584 (4)	0.0471 (2)	0.2197 (2)	3.75 (7)
O(5)	0.2006 (5)	0.2068 (2)	0.3574 (3)	5.01 (9)
O(6)	−0.1484 (4)	0.2324 (2)	0.2366 (2)	4.30 (8)
O(7)	0.1605 (5)	0.2430 (3)	0.1461 (3)	5.4 (1)
N†	0.0565 (18)	0.4840 (10)	1.0435 (8)	8.6 (4)
C	0.1442 (10)	0.4736 (6)	0.9395 (6)	8.1 (2)

† Occupation factors for the Al, Cr and N atoms are 0.5.

Table 2. *Selected bond lengths* (Å) *and angles* (°)

	M = Al	M = Cr
M—O(1)	1.875 (2)	1.959 (2)
M—O(2)	1.891 (2)	1.967 (2)
M—O(3)	1.874 (2)	1.953 (2)
S—O(4)	1.481 (2)	1.476 (2)
S—O(5)	1.459 (2)	1.462 (3)
S—O(6)	1.480 (2)	1.483 (2)
S—O(7)	1.461 (2)	1.464 (3)
N—C	1.39 (1)	1.41 (1)
N—C$^{\rm i}$	1.41 (1)	1.41 (1)
O(1)—M—O(2)	87.6 (1)	87·4 (1)
O(1)—M—O(3)	87.6 (1)	86.9 (1)
O(2)—M—O(3)	91.7 (1)	91.7 (1)
O(4)—S—O(5)	108.9 (1)	108.6 (2)
O(4)—S—O(6)	109.8 (1)	109.6 (1)
O(4)—S—O(7)	109.3 (1)	109.6 (2)
O(5)—S—O(6)	109.3 (1)	109.5 (2)
O(5)—S—O(7)	110.5 (2)	110.6 (2)
O(6)—S—O(7)	109.0 (2)	108.9 (2)
C—N—C$^{\rm i}$	130 (1)	131 (1)

Symmetry code: (i) $-x$, $1 - y$, $-z$.

Discussion. Final atomic parameters for the non-H atoms are listed in Table 1* and selected bond lengths and angles are in Table 2. The ions of the Cr and salt are shown in Fig. 1 (the ions of the Al salt show practically the same arrangement).

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54572 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GE0269]

Our work shows that the Al^{III} and Cr^{III} salts are isostructural, confirming the powder diffraction results (Jordanovska, 1989). The Cr and Al atoms positioned on the symmetry centres are octahedrally coordinated by the O*w* atoms of the water molecules. The weighted means of Al—O*w* and Cr—O*w* bond lengths [1.880 (6) and 1.960 (4) Å, respectively] are in accord with the corresponding averaged bonds from related literature data: 1.875 (Schein, Lingafelter & Stewart, 1967), 1.87 (Lipson, 1935), 1.86 (at 170 K; Fletcher & Steeple, 1964), 1.868 (2) (neutron data; Abdeen, Will & Weiss, 1981), 1.851 (5) and 1.897 (2) (neutron data; Abdeen, Will, Schäfer *et al.*, 1981) and 1.89 Å (Cameron, Chute, Owen, Aherne & Linden, 1990) for the Al—O*w* bonds and 1.954 (Schein *et al.*, 1967) and 1.962 Å (Chesick & Doany, 1981) for the Cr—O*w* bonds. The mean deviations from 90° of O*w*—Al—O*w* and O*w*—Cr—O*w* bond angles are 2.2 (2) and 2.5 (4)°, respectively.

In the disordered dimethylammonium cations the N atoms are displaced from the symmetry centres by 0.59 in (I) and 0.58 Å in (II). Similar disorder near symmetry centres was described for complete cations $(NH_3OH)^+$ (Abdeen, Will & Weiss, 1981), $(NH_3CH_3)^+$ and $(NH_4)^+$ (Abdeen, Will, Schäfer *et al.*, 1981) in three alum structures determined by neutron diffraction.

The sulfate ions are quite regular with mean tetrahedral angles of 109.4 (2) and 109.5 (2)° and mean S—O bond lengths of 1.470 (6) and 1.474 (5) Å for (I) and (II), respectively. In both compounds the O atoms of each sulfate anion participate as acceptors in six strong hydrogen bonds [2.586 (3)–2.676 (3) Å] accepting all water H atoms. The O(7) sulfate atom is also involved in a moderate hydrogen bond [2.86 (1) for (I) and 2.87 (1) Å for (II)] with the dimethylammonium cation accepting one of its H atoms [H(41)], while the H(42) atom does not participate in hydrogen bonding (Table 3). The sulfate O(5) atom, which accepts only one H atom [H(11)], and the O(7) atom which accepts one water H atom and one ammonium H atom show, in both salts, some shorter S—O bonds [1.459 (2)–1.464 (3) Å] than the O(4) and O(6) atoms which each accept two water H atoms, showing S—O bonds in the range 1.476 (2)–1.483 (2) Å.

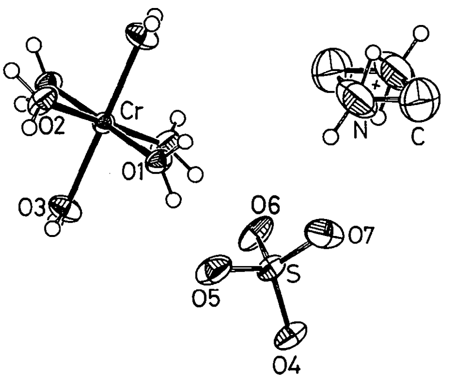

Fig. 1. A view of compound (II) with atom numbering. A symmetry centre near disordered dimethylammonium ions is denoted by *x*. Ellipsoids are at the 50% probability level.

Table 3. *Geometry of the hydrogen bonds* (Å,°)

D	H	*A*	*D*···*A*	*D*—H	H···*A*	*D*—H···*A*
Compound (I)						
O(1)	H(11)	O(5)	2.586 (3)	0.89	1.72	165
O(1)	H(12)	$O(4^{ii})$	2.665 (3)	0.96	1.71	175
O(2)	H(21)	$O(6^{iii})$	2.676 (3)	0.86	1.88	154
O(2)	H(22)	$O(4^{iv})$	2.639 (3)	0.87	1.77	170
O(3)	H(31)	$O(7^{v})$	2.595 (3)	0.88	1.72	172
O(3)	H(32)	$O(6^{iv})$	2.643 (3)	0.76	1.88	175
N	H(41)	O(7)	2.86 (1)	0.89	1.98	168
Compound (II)						
O(1)	H(11)	O(5)	2.588 (3)	0.85	1.77	160
O(1)	H(12)	$O(4^{ii})$	2.673 (3)	0.83	1.85	177
O(2)	H(21)	$O(6^{iii})$	2.643 (3)	0.89	1.76	178
O(2)	H(22)	$O(4^{iv})$	2.638 (3)	0.84	1.81	166
O(3)	H(31)	$O(7^{v})$	2.593 (4)	0.75	1.85	171
O(3)	H(32)	$O(6^{iv})$	2.636 (3)	0.73	1.91	174
N	H(41)	O(7)	2.87 (1)	0.95	2.04	145

Symmetry code: (i) $-x, 1-y, -z$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $-x, 1-y, 1-z$; (iv) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (v) $-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.

The authors thank V. Puntarec for collecting the diffractometer data. This investigation was supported by the Research Council of Croatia

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