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Hemi(piperazinediium) hexaaqua-aluminium(III) bis(sulfate) tetrahydrate: a new double aluminium sulfate salt

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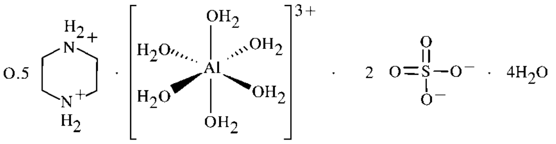
Piperazinium aluminium sulfate decahydrate, $(C_4H_{12}N_2)_{0.5}$-$[Al(H_2O)_6](SO_4)_2 \cdot 4H_2O$, exhibits a crystal structure built from isolated $[Al(H_2O)_6]^{3+}$, SO_4^{2-}, $C_4H_{12}N_2^{2+}$ and H_2O units connected by a complex hydrogen-bond network. The title compound shows strong similarities to many double aluminium sulfates, such as alums and Tutton's salts. However, since its structure is not derived directly from that of these compounds, it is assumed to be a new structure type.

Comment

Studies in sulfate-based chemistry have recently experienced a resurgence in interest, with the use of the SO_4^{2-} anion as a tetrahedral building block and amines as templates (Choudhury *et al.*, 2001; Norquist *et al.*, 2003). The new amine lanthanum sulfates obtained recently (Bataille & Louër, 2002; Xing *et al.*, 2003) also offer a promising route to open structures. Similarly, by using trivalent aluminium, it would be expected that materials with open frameworks constructed only from tetrahedral building units could be prepared. Instead, the crystal structure of the new piperazinium aluminium sulfate decahydrate obtained here, *viz.* $(C_4H_{12}N_2)_{0.5}$-$[Al(H_2O)_6](SO_4)_2 \cdot 4H_2O$, (I), consists of isolated entities linked through a complex hydrogen-bond network. The present work also deals with the similarity of the crystal structure of (I) to those of other double aluminium sulfates, such as Tutton's salts and alums.



(I)

Alums [general formula $A^{I}M^{III}(SO_4)_2 \cdot 12H_2O$] and Tutton's salts [general formula $A^{I}_{2}M^{II}(SO_4)_2 \cdot 6H_2O$] are two large families of double salts that include the sulfate anion. The chemical formula of (I) can be written as $[(C_4H_{12}N_2)_{0.5}]Al$-$(SO_4)_2 \cdot 10H_2O$. Compound (I) is thus related to the alum family, except that *A* is a divalent cation with halved stoichiometry and the compound is decahydrated. Nevertheless, the space-group symmetry of (I) ($P2_1/n$) is comparable to that of dimethylammonium aluminium sulfate hexahydrate ($P2_1/n$; Galešić & Jordanovska, 1992) and Tutton's salts ($P2_1/a$; see, for example, Maslen *et al.*, 1988), while alums crystallize with a cubic symmetry. The structure of (I) (Figs. 1 and 2) consists of Al^{3+} ions octahedrally coordinated to six water molecules, together with sulfate tetrahedra, piperazinium cations (lying about inversion centres) and non-bonded water molecules, linked by hydrogen bonds only. This bonding feature has already been observed in, for example, piperazinium sulfate monohydrate (Jayaraman *et al.*, 2002). The crystal structure of

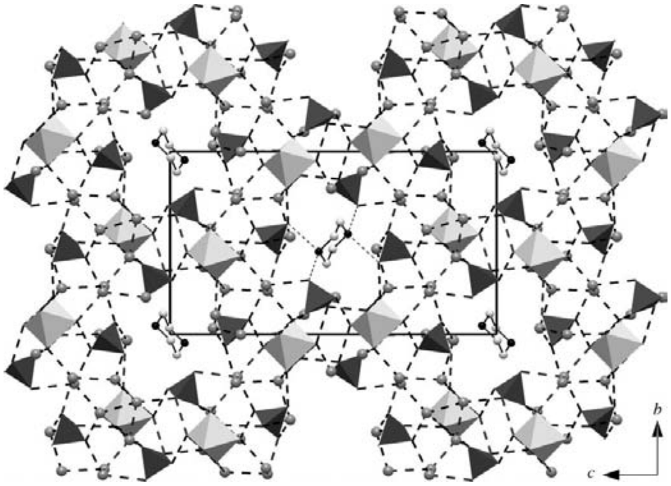


Figure 1
A projection of the structure of (I) along the *a* axis, showing the hydrogen-bond network formed by the $[Al(H_2O)_6]^{3+}$ (light grey octahedra), SO_4^{2-} (dark grey tetrahedra), $C_4H_{12}N_2^{2+}$ and H_2O entities. Hydrogen bonds formed *via* water molecules are represented by thick dashed lines, while hydrogen bonds involving N atoms are shown as thin dashed lines. H atoms have been omitted for clarity.

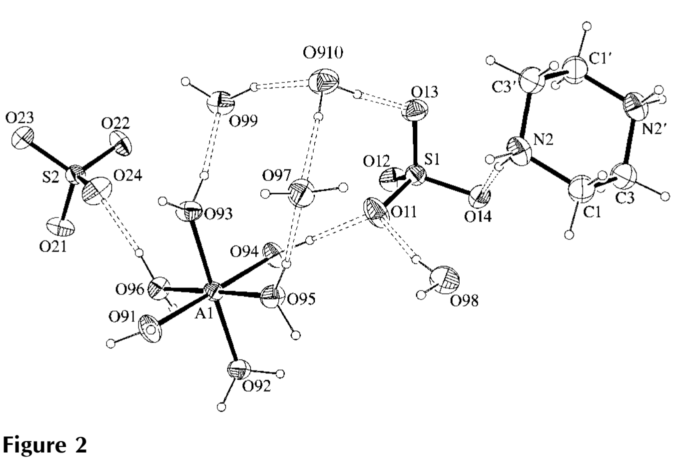


Figure 2
Part of the crystal structure of (I), showing the asymmetric unit and the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are represented by dashed lines. [Symmetry code: (i) $-x, -y, -z$.]

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(I) is unlike that of other double aluminium sulfates, in which the metal atom is located at the origin of the cell, in that the Al atom in (I) lies in a general position. Selected bond lengths are given in Table 1. The Al—O*W* bond lengths range from 1.8620 (17) to 1.8872 (17) Å [mean 1.876 (2) Å], in agreement with the value (1.876 Å) calculated using the bond-valence program *VALENCE* (Brown, 1996) for a sixfold oxygen-coordinated Al atom. The S—O distances fall in the range 1.4611 (17)–1.4809 (17) Å [mean 1.473 (2) Å], which is also comparable to the value (1.474 Å) calculated using the bond-valence method. This bond length agrees with that observed in many Tutton's salts, while it is generally slightly shorter in alums (Petruševski, 1994). No disorder of the amine group is observed, and the centre of the piperazinium group corresponds to the inversion centre of the unit cell. In the dimethylammonium salt (Galešić & Jordanovska, 1992), the amine group is disordered around the inversion centre, and in α-alums, the monovalent $A^{\rm I}$ cations are disordered around the special position 4*b* of space group *Pa*3 (Larson & Cromer, 1967), while in Tutton's salts, the $A^{\rm I}$ cations lie in general positions (Maslen *et al.*, 1988). The presence of a diprotonated amine group and ten water molecules leads to a complex hydrogen-bond network, involving 22 H atoms (Table 2).

Clearly, the crystal structure of (I) has some analogies to those of other double aluminium sulfate salts. Nevertheless, these similarities are not sufficient to allow us to consider (I) as belonging to the known families of double salts, such as alums and Tutton's salts. Rather, it is likely that (I) is the first member of a new family of double aluminium sulfates. It is therefore of interest to investigate further new aluminium sulfates prepared in the presence of diprotonated amines, in order to establish whether similarities exist with (I).

Table 1
Selected interatomic distances (Å).

Al—O93	1.8620 (17)	S1—O14	1.4753 (17)
Al—O92	1.8726 (17)	S2—O24	1.4611 (17)
Al—O91	1.8733 (16)	S2—O23	1.4677 (18)
Al—O96	1.8792 (17)	S2—O22	1.4797 (16)
Al—O94	1.8835 (16)	S2—O21	1.4809 (17)
Al—O95	1.8872 (17)	C1—N2	1.494 (3)
S1—O13	1.4689 (17)	C1—C3	1.512 (4)
S1—O12	1.4715 (17)	N2—C3$^{\rm i}$	1.485 (3)
S1—O11	1.4745 (16)		

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O91—H11···O22$^{\rm ii}$	0.94 (2)	1.70 (2)	2.625 (2)	172 (3)
O91—H12···O99$^{\rm ii}$	0.96 (2)	1.72 (2)	2.670 (2)	174 (3)
O92—H21···O910$^{\rm iii}$	0.94 (2)	1.71 (2)	2.648 (3)	177 (3)
O92—H22···O21$^{\rm iv}$	0.93 (2)	1.72 (2)	2.642 (2)	175 (3)
O93—H31···O14$^{\rm v}$	0.93 (2)	1.67 (2)	2.604 (2)	176 (3)
O93—H32···O99	0.93 (2)	1.73 (2)	2.645 (2)	169 (2)
O94—H41···O11	0.91 (2)	1.71 (2)	2.621 (2)	175 (3)
O94—H42···O21$^{\rm vi}$	0.95 (2)	1.73 (2)	2.671 (2)	177 (3)
O95—H51···O97	0.95 (2)	1.74 (2)	2.672 (2)	170 (3)
O95—H52···O12$^{\rm ii}$	0.96 (2)	1.77 (2)	2.720 (2)	177 (3)
O96—H61···O24	0.94 (2)	1.70 (2)	2.633 (2)	173 (3)
O96—H62···O22$^{\rm vi}$	0.92 (2)	1.78 (2)	2.698 (2)	172 (2)
O97—H71···O12$^{\rm v}$	0.95 (2)	1.90 (2)	2.828 (3)	165 (3)
O97—H72···O23$^{\rm vii}$	0.94 (2)	1.93 (2)	2.864 (3)	171 (3)
O98—H81···O11	0.94 (2)	1.85 (2)	2.783 (2)	169 (3)
O98—H82···O13$^{\rm ii}$	0.93 (2)	1.97 (2)	2.886 (2)	167 (3)
O99—H91···O98$^{\rm v}$	0.93 (2)	1.82 (2)	2.728 (3)	165 (3)
O99—H92···O910	0.96 (2)	1.92 (2)	2.851 (3)	161 (3)
O910—H101···O97	0.95 (2)	1.94 (2)	2.887 (3)	176 (3)
O910—H102···O13	0.95 (2)	1.77 (2)	2.710 (3)	174 (3)
N2—H21N···O23$^{\rm vii}$	0.97 (2)	1.83 (2)	2.796 (3)	173 (3)
N2—H22N···O14	0.98 (2)	1.96 (2)	2.925 (3)	167 (3)

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

Experimental

Single crystals of (I) were obtained by dissolving $Al_2(SO_4)_3 \cdot 18H_2O$ (0.75 mmol) and piperazine hexahydrate (2 mmol) in H_2O (7 ml) acidified with H_2SO_4 (0.5 ml). The resulting clear solution was allowed to stand for two months, until large crystals were obtained. The product was filtered off and washed with a small amount of distilled water, since the crystals appeared to be slightly soluble.

Crystal data

$(C_4H_{12}N_2)_{0.5}[Al(H_2O)_6]$-
$(SO_4)_2 \cdot 4H_2O$
$M_r = 443.32$
Monoclinic, $P2_1/n$
$a = 6.5737$ (1) Å
$b = 12.0671$ (2) Å
$c = 21.5206$ (5) Å
$\beta = 90.0815$ (7)°
$V = 1707.13$ (6) Å^3
$Z = 4$

$D_x = 1.725$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 11 232 reflections
$\theta = 1.0$–27.5°
$\mu = 0.45$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.52 × 0.13 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
$T_{\rm min} = 0.797$, $T_{\rm max} = 0.967$
19 066 measured reflections
3911 independent reflections

2991 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.070$
$\theta_{\rm max} = 27.5°$
$h = -7 \rightarrow 8$
$k = -15 \rightarrow 15$
$l = -27 \rightarrow 27$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.105$
$S = 1.07$
3911 reflections
296 parameters
Only coordinates of H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.047P)^2 + 0.84P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.35$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.47$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0181 (13)

All 26 H atoms were located from difference Fourier syntheses and their positions were refined isotropically, with O—H, C—H and N—H distances restrained to 0.97 (2) Å and H···H distances restrained to 1.55 (3) Å. The atomic displacement parameters of the H atoms were fixed at $1.5U_{\rm eq}$(parent atom).

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN1030). Services for accessing these data are described at the back of the journal.

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