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Langbeinite-type $(NH_4)_2Mn_2(SO_4)_3$

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(S–O) = 0.003 Å
R factor = 0.030
wR factor = 0.071
Data-to-parameter ratio = 11.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The anionic component of the crystal structure of cubic langbeinite-type diammonium dimanganese(II) trisulfate(IV), $(NH_4)_2Mn_2(SO_4)_3$, is a three-dimensional $[Mn_2(SO_4)_3]^{2-}$ network based on SO_4 tetrahedra corner-linked to $Mn^{II}O_6$ octahedra. The charge-balancing ammonium cations occupy the cavities in the network. The pairs of independent Mn and N atoms lie on special positions of site symmetry 3.

Comment

The development of microporous materials has led to investigations of the factors governing the amine-templated syntheses of metal sulfates (Behera *et al.*, 2004). The present report on a new ammonium manganese sulfate, which was obtained unexpectedly in a hydrothermal synthesis intended for this purpose, is a contribution to the limited number of structural studies of inorganic manganese sulfate compounds, such as, for example, $Mn(HSO_4)_2$, $Mn(HSO_4)_2\cdot H_2O$ and $Mn(HSO_4)_2(H_2SO_4)$ (Stiewe *et al.*,1998), $MnSO_4\cdot H_2O$ (Le Fur *et al.*, 1966), $(H_5O_2)[Mn^{III}(H_2O)_2(SO_4)_2]$ (Chang *et al.*, 1983), $MnSO_4\cdot 5H_2O$ (Caminiti *et al.*, 1982), $MnSO_4\cdot H_2O$ (Wildner & Giester, 1991), and $MnSO_4\cdot 4H_2O$ (Held & Bohatý, 2002). The sulfatomanganate(II) dianion can exist as a distinct entity, as noted in histidinium tetraaquadisulfatomanganate (Wojtczak & Jaskólski, 1989) and ethylenediammonium tetraaquadisulfatomanganate (Chaabouni *et al.*, 1996); both salts have monodentate sulfate groups only.

The title compound is a double salt and crystallizes in the langbeinite $[K_2Mg_2(SO_4)_3]$ structure type (Gossner & Koch, 1931; Zemann & Zemann, 1957). Its cubic cell dimensions (10.192 Å) were first reported by Gattow & Zemann (1957). $(NH_4)_2Mn_2(SO_4)_3$ is isotypic with its selenate analog $(NH_4)_2Mn_2(SeO_4)_3$. The latter is obtained by dehydrating the hexahydrate, and forms a solid-solution series with the sulfate (Kohler & Franke, 1964). The chromate analog, $(NH_4)_2Mn_2(CrO_4)_3$ (Cord *et al.*, 1971), is also isotypic with the title compound.

The anionic component of $(NH_4)_2Mn_2(SO_4)_3$ is a three-dimensional network of SO_4 tetrahedra and $Mn^{II}O_6$ octahedra. Each tetrahedron shares its corners with four octahedra; the Mn—O bond lengths in the two $Mn^{II}O_6$ octahedra are very similar (Table 1 and Fig. 1). The ammonium cations occupy the voids of the network and are weakly hydrogen-bonded to it (Table 2).

Experimental

A mixture of manganese(II) sulfate hydrate (0.05 g, 0.3 mmol), oxalic acid dihydrate (0.02 g, 0.2 mmol), *o*-phenylenediamine (0.02 g, 0.2 mmol) and acetonitrile (5 ml) was sealed into a 15 ml Teflon-lined stainless steel bomb, which was then heated at 433 K for 72 h. The bomb was cooled slowly to room temperature to give pale yellow (almost colorless) block-shaped crystals of $(NH_4)_2Mn_2(SO_4)_3$, in about 65% yield.

Crystal data

$(NH_4)_2Mn_2(SO_4)_3$
$M_r = 434.14$
Cubic, $P2_13$
$a = 10.188$ (2) Å
$V = 1057.5$ (4) Å^3
$Z = 4$
$D_x = 2.727$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1534 reflections
$\theta = 3.5$–$21.5°$
$\mu = 3.05$ mm^{-1}
$T = 295$ (2) K
Block, pale yellow
0.14 × 0.08 × 0.05 mm

Data collection

Bruker APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{\min} = 0.584$, $T_{\max} = 0.862$
7327 measured reflections
818 independent reflections
765 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.069$
$\theta_{\max} = 27.4°$
$h = -13 \rightarrow 13$
$k = -12 \rightarrow 13$
$l = -12 \rightarrow 8$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.071$
$S = 1.05$
818 reflections
70 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.043P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.36$ e Å^{-3}
$\Delta\rho_{\min} = -0.35$ e Å^{-3}
Extinction correction: none
Absolute structure: Flack (1983), 342 Friedel pairs
Flack parameter: 0.01 (4)

Table 1
Selected geometric parameters (Å, °).

Mn1—O1	2.164 (3)	S—O1	1.473 (3)
Mn1—O3$^{\rm iii}$	2.169 (3)	S—O2	1.475 (3)
Mn2—O2	2.157 (3)	S—O3	1.462 (3)
Mn2—O4$^{\rm vii}$	2.175 (3)	S—O4	1.467 (3)
O1—Mn1—O1$^{\rm i}$	95.0 (1)	O2—Mn2—O4$^{\rm viii}$	81.6 (1)
O1—Mn1—O3$^{\rm iii}$	88.8 (1)	O2—Mn2—O4$^{\rm ix}$	173.6 (1)
O1—Mn1—O3$^{\rm iv}$	174.2 (1)	O4$^{\rm vii}$—Mn2—O4$^{\rm viii}$	93.2 (1)
O1—Mn1—O1$^{\rm x}$	95.0 (1)	O1—S—O2	110.4 (2)
O1—Mn1—O3$^{\rm v}$	89.1 (1)	O1—S—O3	108.9 (2)
O3$^{\rm iii}$—Mn1—O3$^{\rm iv}$	86.8 (1)	O1—S—O4	110.7 (2)
O2—Mn2—O2$^{\rm vi}$	94.6 (1)	O2—S—O3	110.6 (2)
O2—Mn2—O2$^{\rm v}$	94.6 (1)	O2—S—O4	107.9 (2)
O2—Mn2—O4$^{\rm vii}$	90.9 (1)	O3—S—O4	108.4 (2)

Symmetry codes: (i) z, x, y; (iii) $-x+2, y+\frac{1}{2}, -z+\frac{3}{2}$; (iv) $-z+\frac{3}{2}, -x+2, y+\frac{1}{2}$; (v) $y+\frac{1}{2}, -z+\frac{3}{2}, -x+2$; (vi) $-z+2, x-\frac{1}{2}, -y+\frac{3}{2}$; (vii) $-x+\frac{3}{2}, -y+1, z+\frac{1}{2}$; (viii) $-z+\frac{3}{2}, -x+1, y+\frac{1}{2}$; (ix) $-y+\frac{3}{2}, -z+1, x+\frac{1}{2}$; (x) y, z, x.

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H11⋯O1$^{\rm v}$	0.85 (1)	2.55 (3)	2.933 (4)	108 (3)
N1—H11⋯O3$^{\rm iii}$	0.85 (1)	2.62 (8)	3.075 (3)	115 (6)
N1—H11⋯O4$^{\rm iii}$	0.85 (1)	2.42 (2)	3.178 (5)	149 (4)
N1—H12⋯O1	0.85 (1)	2.58 (1)	2.933 (4)	106 (1)
N2—H21⋯O2	0.85 (1)	2.12 (1)	2.946 (4)	163 (3)
N2—H22⋯O3$^{\rm x}$	0.85 (1)	2.46 (1)	3.127 (6)	136 (2)

Symmetry codes: (iii) $-x+2, y+\frac{1}{2}, -z+\frac{3}{2}$; (v) $y+\frac{1}{2}, -z+\frac{3}{2}, -x+2$; (x) y, z, x.

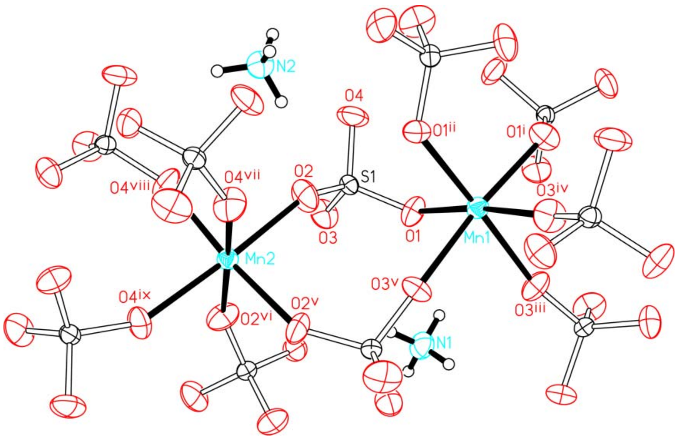

Figure 1
ORTEPII (Johnson, 1976) plot of a part of the structure of $(NH_4)_2Mn_2(SO_4)_3$, with displacement ellipsoids at the 50% probability level. H atoms are drawn as spheres of arbitrary radii. [Symmetry codes: (i) z, x, y; (ii) y, z, x; (iii) $2-x, \frac{1}{2}+y, \frac{3}{2}-z$; (iv) $\frac{3}{2}-z, 2-x, \frac{1}{2}+y$; (v) $\frac{1}{2}+y, \frac{3}{2}-z, 2-x$; (vi) $2-z, x-\frac{1}{2}, \frac{3}{2}-y$; (vii) $\frac{3}{2}-x, 1-y, \frac{1}{2}+z$; (viii) $\frac{3}{2}-z, 1-x, \frac{1}{2}+y$; (ix) $\frac{3}{2}-y, 1-z, \frac{1}{2}+x$.]

H atoms were found in difference Fourier maps and were refined with distance restraints of N—H = 0.85 (1) Å and H⋯H = 1.39 (1) Å. The $U_{\rm iso}$(H) values were set to $1.2U_{\rm eq}$ of the parent atoms.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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