

catena-Poly[[dihydraziniummanganese(II)]-di- μ -sulfato- κ^4 O:O'] from synchrotron data

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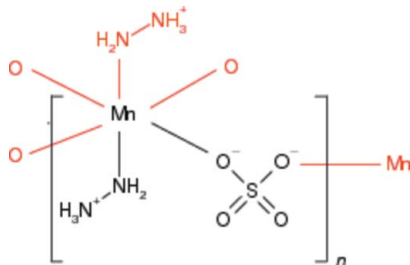
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Key indicators: single-crystal synchrotron study; $T = 120$ K; mean $\sigma(\text{N}—\text{N}) = 0.003$ Å; R factor = 0.082; wR factor = 0.248; data-to-parameter ratio = 12.4.

The title compound, $[\text{Mn}(\text{N}_2\text{H}_5)_2(\text{SO}_4)_2]_n$, contains fairly regular *trans*- MnN_2O_4 octahedra. The Mn atoms (site symmetry $\bar{1}$) are bridged by pairs of sulfate groups into infinite [100] chains, which are cross-linked by a network of $\text{N}—\text{H} \cdots \text{O}$ hydrogen bonds arising from the hydrazinium groups. $\text{Mn}(\text{N}_2\text{H}_5)_2(\text{SO}_4)_2$ is isostructural with its iron, zinc, chromium and cadmium-containing analogues.

Related literature

For isostructural compounds, see: Prout & Powell (1961); Parkins *et al.* (2001); Srinivasan *et al.* (2006); Srinivasan *et al.* (2007).



Experimental

Crystal data

$\text{Mn}(\text{N}_2\text{H}_5)_2(\text{SO}_4)_2$

$M_r = 313.18$

Triclinic, $P\bar{1}$

$a = 5.391$ (1) Å

$b = 5.8678$ (11) Å

$c = 7.3954$ (14) Å

$\alpha = 92.651$ (2)°

$\beta = 104.332$ (2)°

$\gamma = 99.249$ (2)°

$V = 222.81$ (7) Å³

$Z = 1$

Synchrotron radiation

$\lambda = 0.6905$ Å

$\mu = 1.99$ mm^{−1}

$T = 120$ (2) K

$0.02 \times 0.02 \times 0.001$ mm

Data collection

Bruker SMART 1000 CCD

diffractometer

Absorption correction: multi-scan

(*SADABS*; Bruker, 2004)

$T_{\min} = 0.961$, $T_{\max} = 0.998$

1414 measured reflections

881 independent reflections

852 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.082$

$wR(F^2) = 0.248$

$S = 1.23$

881 reflections

71 parameters

H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.73$ e Å^{−3}

$\Delta\rho_{\text{min}} = -1.06$ e Å^{−3}

Table 1

Selected bond lengths (Å).

Mn1—O2 ⁱ	2.1712 (19)	Mn1—N1	2.259 (2)
Mn1—O1	2.1752 (18)		

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

Table 2

Hydrogen-bond geometry (Å, °).

$D—H \cdots A$	$D—H$	$H \cdots A$	$D \cdots A$	$D—H \cdots A$
N1—H1A \cdots O3 ⁱⁱ	0.92	2.27	3.014 (3)	137
N1—H1B \cdots O4 ⁱⁱⁱ	0.92	2.02	2.879 (3)	154
N2—H2A \cdots O4 ⁱⁱ	0.91	1.91	2.794 (3)	165
N2—H2B \cdots O3	0.91	1.92	2.755 (3)	152
N2—H2C \cdots O2 ⁱ	0.91	2.41	2.882 (3)	112
N2—H2C \cdots O2 ⁱⁱⁱ	0.91	2.36	2.988 (3)	126
N2—H2C \cdots O1 ^{iv}	0.91	2.38	3.110 (3)	137

Symmetry codes: (i) $-x + 1, -y, -z$; (ii) $-x + 1, -y, -z + 1$; (iii) $x - 1, y - 1, z$; (iv) $x, y - 1, z$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2112).

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supplementary materials

Acta Cryst. (2007). E63, i152 [doi:10.1107/S1600536807024579]

***catena*-Poly[[dihydraziniummanganese(II)]-di- μ -sulfato- κ^4 O:O'] from synchrotron data**

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Comment

The title compound, (I), was prepared as part of our ongoing structural studies of the $M^{\text{II}}(\text{N}_2\text{H}_5)_2(\text{SO}_4)_2$ family of compounds. It is isostructural with its iron (Srinivasan *et al.*, 2007), cadmium (Srinivasan *et al.*, 2006), chromium (Parkins *et al.*, 2001) and zinc (Prout & Powell, 1961) analogues. The extremely thin plates of (I) necessitated the use of synchrotron radiation for the data collection.

Compound (I) contains *trans*- MnN_2O_4 octahedra (Fig. 1, Table 1), where the bonded N atom is part of a hydrazinium (N_2H_5^+) cation. The Mn atoms (site symmetry $\bar{1}$) are connected by pairs of sulfate groups into infinite chains that propagate in [100]. The intra-chain Mn \cdots Mn separation in (I) is equal to 5.391 (1) Å, the a unit-cell dimension.

The manganese-sulfate chains in (I) are crosslinked by N—H \cdots O hydrogen bonds (Table 2) to result in the same hydrogen bonding network as that seen in the analogues noted above, including a trifurcated N2—H3c \cdots (O,O,O) link (mean bond angle about H3c = 108°).

Experimental

The reaction of hydrazine hydrate ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$; 0.50 g, 10 mmol) and ethyl bromoacetate (1.671 g, 10 mmol) in 5 ml of dry ethanol resulted in the formation of a white solid containing hydrazinium bromide and ethyl hydrazinoacetate, as reported earlier (Srinivasan *et al.*, 2006). This white solid (0.236 g) was dissolved in water (30 ml) and mixed with an aqueous solution (30 ml) of $\text{MnSO}_4\cdot\text{H}_2\text{O}$ (0.169 g, 1 mmol) in few drops of conc. H_2SO_4 . The resulting clear solution, with a pH of 2, was concentrated over a water bath to 20 ml and kept for crystallization at room temperature. After 5 days, colourless clumps of very thin plates of (I) were formed. These were recovered by filtration, washed with cold water and dried in air.

Refinement

Although more than a hemisphere of intensity data was scanned, the low data completion is thought to have arisen from as-yet unresolved problems in the data-reduction software. The H atoms were positioned geometrically (N—H = 0.91–0.92 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$. The deepest difference hole is 1.49 Å from H2a.

Figures

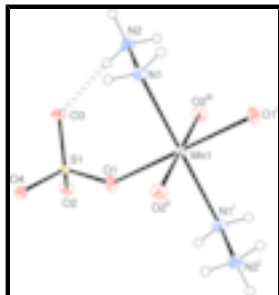


Fig. 1. View of the molecular structure of (I) expanded to show the manganese coordination sphere (50% displacement ellipsoids; arbitrary spheres for the H atoms). Symmetry codes: (i) $-x, -y, -z$; (ii) $x - 1, y, z$; (iii) $1 - x, -y, -z$. The double-dashed line represents the hydrogen bond.

catena-poly[[dihydriziniummanganese(II)]-di- μ -sulfato- κ^4 O:O']

Crystal data

$\text{Mn}(\text{N}_2\text{H}_5)_2(\text{SO}_4)_2$	$V = 222.81 (7) \text{ \AA}^3$
$M_r = 313.18$	$Z = 1$
Triclinic, $P\bar{1}$	$F_{000} = 159$
Hall symbol: $-P\ 1$	$D_x = 2.334 \text{ Mg m}^{-3}$
$a = 5.391 (1) \text{ \AA}$	Synchrotron radiation
$b = 5.8678 (11) \text{ \AA}$	$\lambda = 0.69050 \text{ \AA}$
$c = 7.3954 (14) \text{ \AA}$	$\mu = 1.99 \text{ mm}^{-1}$
$\alpha = 92.651 (2)^\circ$	$T = 120 (2) \text{ K}$
$\beta = 104.332 (2)^\circ$	Plate, colourless
$\gamma = 99.249 (2)^\circ$	$0.02 \times 0.02 \times 0.001 \text{ mm}$

Data collection

Bruker SMART 1000 CCD diffractometer	881 independent reflections
Radiation source: beam line 9.8 at Daresbury synchrotron	852 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.027$
$T = 120(2) \text{ K}$	$\theta_{\text{max}} = 29.7^\circ$
ω scans	$\theta_{\text{min}} = 3.9^\circ$
Absorption correction: multi-scan (SADABS; Bruker, 2004)	$h = -7 \rightarrow 7$
$T_{\text{min}} = 0.961, T_{\text{max}} = 0.998$	$k = -8 \rightarrow 8$
1414 measured reflections	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.082$	H-atom parameters constrained

$wR(F^2) = 0.248$	$w = 1/[\sigma^2(F_o^2) + (0.2P)^2]$
$S = 1.23$	where $P = (F_o^2 + 2F_c^2)/3$
881 reflections	$(\Delta/\sigma)_{\max} < 0.001$
71 parameters	$\Delta\rho_{\max} = 0.73 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\min} = -1.06 \text{ e } \text{\AA}^{-3}$
	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Mn1	0.0000	0.0000	0.0000	0.0057 (5)
S1	0.63753 (11)	0.24939 (10)	0.22017 (8)	0.0049 (5)
O1	0.3752 (4)	0.2300 (3)	0.0925 (3)	0.0112 (6)
O2	0.8345 (4)	0.2732 (3)	0.1091 (3)	0.0082 (6)
O3	0.6580 (4)	0.0439 (3)	0.3271 (3)	0.0098 (6)
O4	0.6915 (4)	0.4609 (3)	0.3504 (3)	0.0081 (6)
N1	0.0682 (4)	-0.1820 (4)	0.2659 (3)	0.0073 (6)
H1A	0.1181	-0.0716	0.3665	0.009*
H1B	-0.0870	-0.2701	0.2709	0.009*
N2	0.2616 (5)	-0.3304 (4)	0.2857 (3)	0.0089 (6)
H2A	0.2730	-0.3998	0.3943	0.011*
H2B	0.4187	-0.2440	0.2883	0.011*
H2C	0.2146	-0.4408	0.1871	0.011*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0062 (6)	0.0061 (6)	0.0046 (6)	0.0002 (4)	0.0013 (4)	0.0010 (3)
S1	0.0056 (6)	0.0052 (6)	0.0039 (7)	-0.0009 (4)	0.0023 (4)	0.0001 (4)
O1	0.0065 (10)	0.0126 (10)	0.0115 (12)	-0.0026 (7)	-0.0006 (8)	0.0011 (8)
O2	0.0095 (9)	0.0097 (10)	0.0075 (10)	-0.0005 (7)	0.0075 (7)	0.0011 (7)
O3	0.0131 (10)	0.0075 (10)	0.0090 (11)	0.0002 (7)	0.0035 (8)	0.0037 (7)
O4	0.0115 (9)	0.0070 (10)	0.0055 (10)	0.0000 (7)	0.0029 (7)	-0.0005 (7)
N1	0.0071 (10)	0.0084 (11)	0.0081 (11)	0.0022 (8)	0.0042 (8)	0.0018 (8)
N2	0.0111 (11)	0.0087 (11)	0.0070 (12)	0.0018 (8)	0.0026 (8)	0.0014 (7)

Geometric parameters (\AA , $^\circ$)

Mn1—O2 ⁱ	2.1712 (19)	S1—O2	1.489 (2)
Mn1—O2 ⁱⁱ	2.1712 (19)	O2—Mn1 ^{iv}	2.1712 (19)
Mn1—O1 ⁱⁱⁱ	2.1752 (18)	N1—N2	1.447 (3)
Mn1—O1	2.1752 (18)	N1—H1A	0.9200
Mn1—N1	2.259 (2)	N1—H1B	0.9200
Mn1—N1 ⁱⁱⁱ	2.259 (2)	N2—H2A	0.9100
S1—O3	1.4765 (19)	N2—H2B	0.9100
S1—O1	1.4772 (19)	N2—H2C	0.9100
S1—O4	1.4787 (19)		
O2 ⁱ —Mn1—O2 ⁱⁱ	180.0	O3—S1—O2	109.51 (11)
O2 ⁱ —Mn1—O1 ⁱⁱⁱ	87.22 (7)	O1—S1—O2	109.35 (12)
O2 ⁱⁱ —Mn1—O1 ⁱⁱⁱ	92.78 (7)	O4—S1—O2	107.99 (11)
O2 ⁱ —Mn1—O1	92.78 (7)	S1—O1—Mn1	142.28 (13)
O2 ⁱⁱ —Mn1—O1	87.22 (7)	S1—O2—Mn1 ^{iv}	127.72 (11)
O1 ⁱⁱⁱ —Mn1—O1	180.0	N2—N1—Mn1	115.31 (15)
O2 ⁱ —Mn1—N1	84.77 (8)	N2—N1—H1A	108.4
O2 ⁱⁱ —Mn1—N1	95.23 (8)	Mn1—N1—H1A	108.4
O1 ⁱⁱⁱ —Mn1—N1	87.42 (8)	N2—N1—H1B	108.4
O1—Mn1—N1	92.58 (8)	Mn1—N1—H1B	108.4
O2 ⁱ —Mn1—N1 ⁱⁱⁱ	95.23 (8)	H1A—N1—H1B	107.5
O2 ⁱⁱ —Mn1—N1 ⁱⁱⁱ	84.77 (8)	N1—N2—H2A	109.5
O1 ⁱⁱⁱ —Mn1—N1 ⁱⁱⁱ	92.58 (8)	N1—N2—H2B	109.5
O1—Mn1—N1 ⁱⁱⁱ	87.42 (8)	H2A—N2—H2B	109.5
N1—Mn1—N1 ⁱⁱⁱ	180.0	N1—N2—H2C	109.5
O3—S1—O1	111.04 (11)	H2A—N2—H2C	109.5
O3—S1—O4	109.90 (11)	H2B—N2—H2C	109.5
O1—S1—O4	108.98 (13)		
O3—S1—O1—Mn1	−1.2 (3)	O3—S1—O2—Mn1 ^{iv}	27.96 (18)
O4—S1—O1—Mn1	−122.4 (2)	O1—S1—O2—Mn1 ^{iv}	−93.92 (16)
O2—S1—O1—Mn1	119.8 (2)	O4—S1—O2—Mn1 ^{iv}	147.62 (14)
O2 ⁱ —Mn1—O1—S1	−61.4 (2)	O2 ⁱ —Mn1—N1—N2	21.43 (16)
O2 ⁱⁱ —Mn1—O1—S1	118.6 (2)	O2 ⁱⁱ —Mn1—N1—N2	−158.57 (16)
N1—Mn1—O1—S1	23.5 (2)	O1 ⁱⁱⁱ —Mn1—N1—N2	108.87 (17)
N1 ⁱⁱⁱ —Mn1—O1—S1	−156.5 (2)	O1—Mn1—N1—N2	−71.13 (17)

Symmetry codes: (i) $-x+1, -y, -z$; (ii) $x-1, y, z$; (iii) $-x, -y, -z$; (iv) $x+1, y, z$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A \cdots O3 ^v	0.92	2.27	3.014 (3)	137

N1—H1B···O4 ^{vi}	0.92	2.02	2.879 (3)	154
N2—H2A···O4 ^v	0.91	1.91	2.794 (3)	165
N2—H2B···O3	0.91	1.92	2.755 (3)	152
N2—H2C···O2 ⁱ	0.91	2.41	2.882 (3)	112
N2—H2C···O2 ^{vi}	0.91	2.36	2.988 (3)	126
N2—H2C···O1 ^{vii}	0.91	2.38	3.110 (3)	137

Symmetry codes: (v) $-x+1, -y, -z+1$; (vi) $x-1, y-1, z$; (i) $-x+1, -y, -z$; (vii) $x, y-1, z$.

Fig. 1

