Crystal structure of hexakis(dimethyl sulfoxide-κO)-manganese(II) tetraiodide

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The title salt, $[Mn(C_2H_6OS)_6]I_4$, is made up from discrete $[Mn(DMSO)_6]^{2+}$ (DMSO is dimethyl sulfoxide) units connected through non-classical hydrogen bonds to linear I_4^{2-} tetraiodide anions. The Mn^{II} ion in the cation, situated on a position with site symmetry $\bar{3}$., is octahedrally coordinated by O atoms of the DMSO molecule with an Mn—O distance of 2.1808 (12) Å. The I_4^{2-} anion contains a neutral I_2 molecule weakly coordinated by two iodide ions, forming a linear centrosymmetric tetraiodide anion. The title compound is isotypic with the Co, Ni, Cu, and Zn analogues.

1. Chemical context

Inorganic–organic hybrid compounds have attracted significant attention owing to their fascinating structural, optical and electrical properties (Stranks & Snaith, 2015). In particular, $CH_3NH_3PbX_3$ hybrids obtained from PbX_2 and CH_3NH_3X (X = I, Br, Cl) are interesting due to their high absorption coefficient and applications in optoelectronics (Stoumpos & Kanatzidis, 2015). In general, this family of materials adopts the perovskite ABX_3 structure type, where A is an organic cation, which is surrounded by twelve nearest X halide anions, and B is a metal cation (Grätzel, 2014). There are continuous efforts on replacing Pb in these hybrids due to its toxicity (Wang *et al.*, 2015). In the present work, one such attempt was made to produce a hybrid between CH_3NH_3I and MnI_2. However, we obtained instead the title salt $[Mn(DMSO)_6]I_4$ (DMSO is dimethyl sulfoxide), and report here its crystal structure.
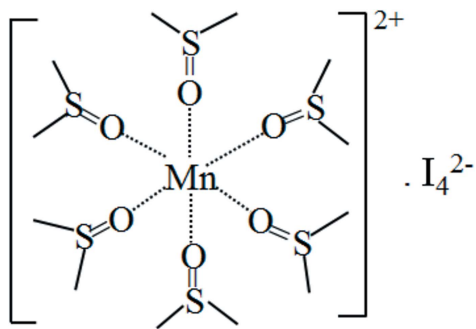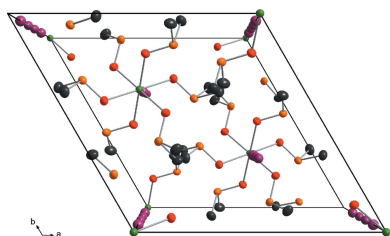
2. Structural commentary

The title salt is the first compound with a $[Mn(DMSO]^{2+}$ cation and a linear tetraiodide anion. The Mn^{2+} cation is
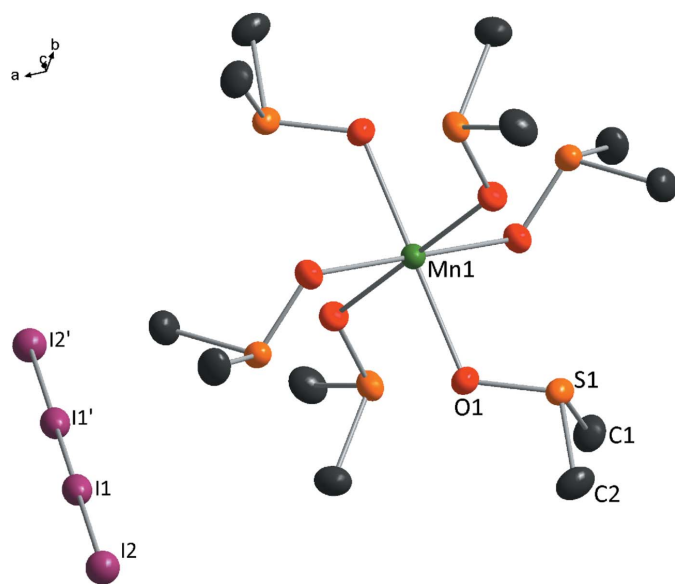
Figure 1
The molecular components of the title compound, with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity. [Symmetry code: (') $\frac{4}{3} - x, \frac{2}{3} - y, \frac{5}{3} - z$.]

bound to the O atoms of six DMSO molecules arranged in an octahedral configuration (Fig. 1). Owing to the $\bar{3}$. site symmetry of the metal cation, the deviations of corresponding angles from ideal values are minute [range *cis* O—Mn—O angles 86.28 (4)–93.73 (4)°; all *trans* angles 180°]. The Mn—O bond length is 2.1808 (12) Å. The four I atoms are arranged in a linear fashion. The bond length between the two central I atoms is 2.8460 (5) Å; this inner I_2 moiety is rather weakly bonded to two terminal I^- anions with a bond lengths of 3.3251 (6) Å. This confirms the existence of a linear, centro-symmetric polyiodide ion I_4^{2-}, consistent with previous reports (Long *et al.*, 1999). Both inner and terminal bond lengths of the I_4^{2-} anion are comparable with values found in [Cu(NH$_3$)$_4$]I$_4$ (Dubler & Linowsky, 1975) or other [M(DMSO)$_6$]I$_4$ compounds (Long *et al.*, 1999; Tkachev *et al.*, 1994; Garzón-Tovar *et al.*, 2013a,b).
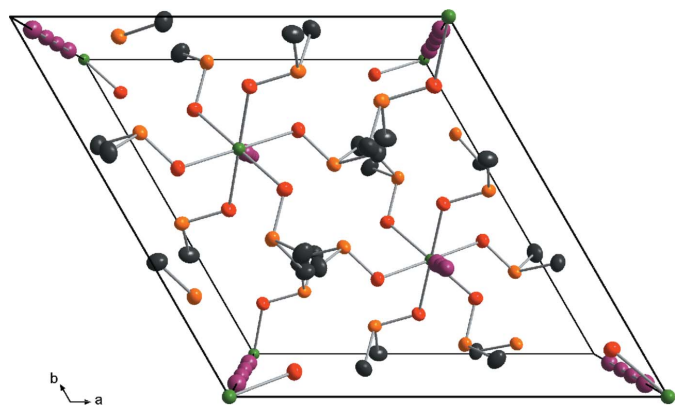

Figure 2
The unit cell of [Mn(DMSO)$_6$]I$_4$ in a view approximately along [001]. H atoms have been omitted for clarity.

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C1—H1A⋯I2	0.98	3.10	3.954 (2)	147
C2—H2B⋯I1^i	0.98	3.26	4.182 (2)	158
C2—H2C⋯I2^{ii}	0.98	3.20	4.108 (2)	154

Symmetry codes: (i) $-x + \frac{5}{3}, -y + \frac{4}{3}, -z + \frac{4}{3}$; (ii) $-x + 1, -y + 1, -z + 1$.

3. Supramolecular features

Fig. 2 shows the unit-cell projection along [001]. The hexagonal rod packing of isolated [Mn(DMSO)$_6$]$^{2+}$ molecules can be seen along [211]. The tetraiodide counter-anions are located between the rows (Fig. 3). An extended three-dimensional supramolecular network is accomplished through non-classical hydrogen bonding between H atoms of the DMSO molecules and the linear I_4^{2-} polyiodide anions. Table 1 collates numerical details of these C—H⋯I interactions.

4. Database survey

A number of transition metals have been reported to form complexes with DMSO (Meek *et al.*, 1960). However, reports on Mn complexes of DMSO with halide anions are scarce, as revealed by a search in the Cambridge Structural Database (Groom *et al.* 2016). Recently Glatz *et al.* (2016) reported the crystal structure of [Mn(DMSO)$_6$]I$_2$. In particular, polyiodide salts are interesting compounds owing to their high conductivity and non-linear properties that are predominantly observed in sulfur-rich compounds (Long *et al.*, 1999). The structure of the title compound is isotypic with the Co, Ni, Cu,
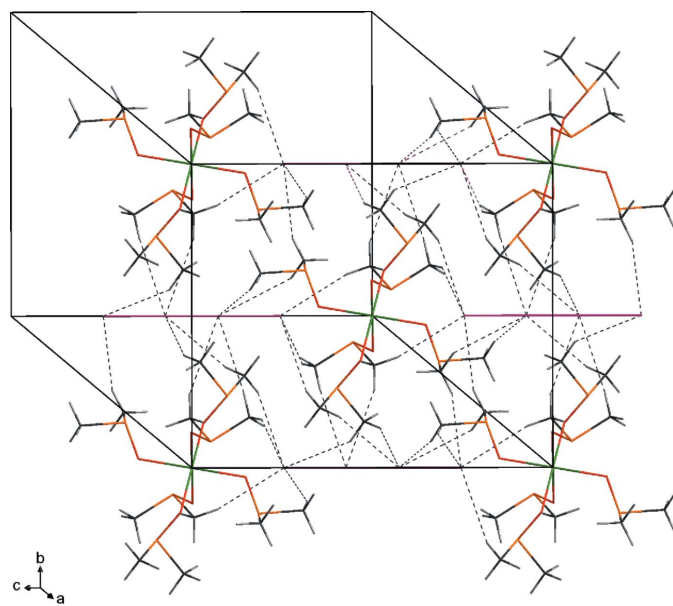

Figure 3
Packing diagram of the title compound. Non-classical hydrogen bonds are shown as dashed lines.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Mn(C_2H_6OS)_6]I_4$
M_r	1031.31
Crystal system, space group	Trigonal, $R\bar{3}$
Temperature (K)	200
a, c (Å)	11.8702 (10), 19.3860 (18)
V (Å^3)	2365.6 (5)
Z	3
Radiation type	Mo $K\alpha$
μ (mm^{-1})	4.75
Crystal size (mm)	$0.16 \times 0.12 \times 0.05$
Data collection	
Diffractometer	Stoe IPDS2
Absorption correction	Numerical (X-RED32; Stoe & Cie, 2013)
T_{min}, T_{max}	0.415, 0.615
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7644, 1417, 1301
R_{int}	0.045
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.685
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.017, 0.038, 1.06
No. of reflections	1417
No. of parameters	47
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.34, −0.93

Computer programs: X-AREA and X-RED32 (Stoe & Cie, 2013), SHELXT (Sheldrick, 2015a), SHELXL2014 (Sheldrick, 2015b), DIAMOND (Brandenburg, 2006) and publCIF (Westrip, 2010).

and Zn analogues: $[Co(DMSO)_6]I_4$ (Tkachev et al., 1994), $[Ni(DMSO)_6]I_4$ (Long et al., 1999), $[Cu(DMSO)_6]I_4$ (Garzón-Tovar et al., 2013a), $[Zn(DMSO)_6]I_4$ (Garzón-Tovar et al., 2013b).

5. Synthesis and crystallization

The title manganese salt was formed in the course of the targeted synthesis of a hybrid compound between CH_3NH_3I and MnI_2. Anhydrous MnI_2 and dimethyl sulfoxide (DMSO) were purchased from Alfa–Aesar and Sigma–Aldrich, respectively. CH_3NH_3I was purchased from Dyesol. The precursors were used without further purification. The title manganese salt was synthesized by adding anhydrous MnI_2 (308.7 mg) and CH_3NH_3I (158.9 mg) in a glass vial. Then 2 ml DMSO was added to the vial (capped afterwards) and stirred at 353 K for 24 h inside a nitrogen glove box. A reddish-black solution was observed after 24 h which was cooled down to room temperature and left for 7 d undisturbed. Single crystals of the title compound were obtained as the only solid product after 7 d. The crystals were removed from the vial and dried under nitrogen flow.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The methyl H atoms were treated as riding and $U_{iso}(H)$ values set at $1.5U_{eq}(C)$.

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supporting information

Crystal structure of hexakis(dimethyl sulfoxide-*κO*)manganese(II) tetraiodide

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Computing details

Data collection: *X-AREA* (Stoe & Cie, 2013); cell refinement: *X-AREA* (Stoe & Cie, 2013); data reduction: *X-RED32* (Stoe & Cie, 2013); program(s) used to solve structure: SHELXT (Sheldrick, 2015*a*); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015*b*); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Hexakis(dimethyl sulfoxide-*κO*)manganese(II) tetraiodide

Crystal data

$[Mn(C_2H_6OS)_6]I_4$	$D_x = 2.172$ Mg m^{-3}
$M_r = 1031.31$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Trigonal, $R\bar{3}{:}H$	Cell parameters from 10442 reflections
$a = 11.8702$ (10) Å	$\theta = 2.2$–$29.5°$
$c = 19.3860$ (18) Å	$\mu = 4.75$ mm^{-1}
$V = 2365.6$ (5) Å^3	$T = 200$ K
$Z = 3$	Block, brown
$F(000) = 1467$	$0.16 \times 0.12 \times 0.05$ mm

Data collection

Stoe IPDS-2 diffractometer	7644 measured reflections
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus	1417 independent reflections
	1301 reflections with $I > 2\sigma(I)$
Detector resolution: 6.67 pixels mm^{-1}	$R_{int} = 0.045$
rotation method scans	$\theta_{max} = 29.2°$, $\theta_{min} = 2.2°$
Absorption correction: numerical (*X-RED32*; Stoe & Cie, 2013)	$h = -16 \rightarrow 16$
	$k = -16 \rightarrow 16$
$T_{min} = 0.415$, $T_{max} = 0.615$	$l = -26 \rightarrow 26$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.017$	
$wR(F^2) = 0.038$	$w = 1/[\sigma^2(F_o^2) + (0.0105P)^2 + 3.7009P]$
$S = 1.06$	where $P = (F_o^2 + 2F_c^2)/3$
1417 reflections	$(\Delta/\sigma)_{max} = 0.001$
47 parameters	$\Delta\rho_{max} = 0.34$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.93$ e Å^{-3}

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Mn1	0.3333	0.6667	0.6667	0.01931 (12)
I1	0.6667	0.3333	0.75993 (2)	0.03170 (6)
I2	0.6667	0.3333	0.58841 (2)	0.03067 (6)
S1	0.54925 (4)	0.62436 (4)	0.58993 (2)	0.02341 (9)
O1	0.50872 (12)	0.72442 (12)	0.60608 (6)	0.0247 (2)
C1	0.67639 (18)	0.65612 (19)	0.64912 (11)	0.0325 (4)
H1A	0.7149	0.6023	0.6373	0.049*
H1B	0.6410	0.6353	0.6960	0.049*
H1C	0.7433	0.7482	0.6466	0.049*
C2	0.64415 (19)	0.6821 (2)	0.51353 (10)	0.0343 (4)
H2A	0.6785	0.6249	0.5015	0.051*
H2B	0.7165	0.7706	0.5212	0.051*
H2C	0.5897	0.6829	0.4757	0.051*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.01701 (16)	0.01701 (16)	0.0239 (3)	0.00851 (8)	0.000	0.000
I1	0.02446 (7)	0.02446 (7)	0.04619 (13)	0.01223 (4)	0.000	0.000
I2	0.03185 (8)	0.03185 (8)	0.02833 (10)	0.01592 (4)	0.000	0.000
S1	0.01918 (17)	0.02122 (18)	0.0279 (2)	0.00868 (15)	0.00044 (15)	−0.00439 (15)
O1	0.0219 (5)	0.0245 (6)	0.0294 (6)	0.0128 (5)	0.0038 (5)	0.0002 (5)
C1	0.0318 (9)	0.0368 (10)	0.0344 (9)	0.0212 (8)	−0.0054 (8)	−0.0033 (8)
C2	0.0298 (9)	0.0447 (11)	0.0283 (9)	0.0185 (9)	0.0040 (7)	−0.0047 (8)

Geometric parameters (Å, º)

Mn1—O1[i]	2.1808 (12)	S1—C2	1.778 (2)
Mn1—O1[ii]	2.1808 (12)	S1—C1	1.7798 (19)
Mn1—O1[iii]	2.1808 (12)	C1—H1A	0.9800
Mn1—O1[iv]	2.1808 (12)	C1—H1B	0.9800
Mn1—O1[v]	2.1809 (12)	C1—H1C	0.9800
Mn1—O1	2.1808 (12)	C2—H2A	0.9800
I1—I1[vi]	2.8460 (5)	C2—H2B	0.9800
S1—O1	1.5204 (12)	C2—H2C	0.9800
O1[i]—Mn1—O1[ii]	180.00 (6)	O1—S1—C1	105.53 (9)
O1[i]—Mn1—O1[iii]	86.27 (4)	C2—S1—C1	98.56 (10)
O1[ii]—Mn1—O1[iii]	93.73 (4)	S1—O1—Mn1	119.38 (7)

O1^i—Mn1—O1^{iv}	93.73 (4)	S1—C1—H1A	109.5
O1^{ii}—Mn1—O1^{iv}	86.27 (4)	S1—C1—H1B	109.5
O1^{iii}—Mn1—O1^{iv}	180.00 (5)	H1A—C1—H1B	109.5
O1^i—Mn1—O1^v	93.73 (4)	S1—C1—H1C	109.5
O1^{ii}—Mn1—O1^v	86.27 (4)	H1A—C1—H1C	109.5
O1^{iii}—Mn1—O1^v	86.27 (5)	H1B—C1—H1C	109.5
O1^{iv}—Mn1—O1^v	93.72 (4)	S1—C2—H2A	109.5
O1^i—Mn1—O1	86.28 (4)	S1—C2—H2B	109.5
O1^{ii}—Mn1—O1	93.73 (4)	H2A—C2—H2B	109.5
O1^{iii}—Mn1—O1	93.73 (4)	S1—C2—H2C	109.5
O1^{iv}—Mn1—O1	86.27 (5)	H2A—C2—H2C	109.5
O1^v—Mn1—O1	180.0	H2B—C2—H2C	109.5
O1—S1—C2	104.90 (9)		

Symmetry codes: (i) $y-1/3$, $-x+y+1/3$, $-z+4/3$; (ii) $-y+1$, $x-y+1$, z; (iii) $-x+y$, $-x+1$, z; (iv) $x-y+2/3$, $x+1/3$, $-z+4/3$; (v) $-x+2/3$, $-y+4/3$, $-z+4/3$; (vi) $-x+4/3$, $-y+2/3$, $-z+5/3$.

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1*A*···I2	0.98	3.10	3.954 (2)	147
C2—H2*B*···I1^{vii}	0.98	3.26	4.182 (2)	158
C2—H2*C*···I2^{viii}	0.98	3.20	4.108 (2)	154

Symmetry codes: (vii) $-x+5/3$, $-y+4/3$, $-z+4/3$; (viii) $-x+1$, $-y+1$, $-z+1$.