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Hexakis(dimethyl sulfoxide-κO)zinc(II) polyiodide

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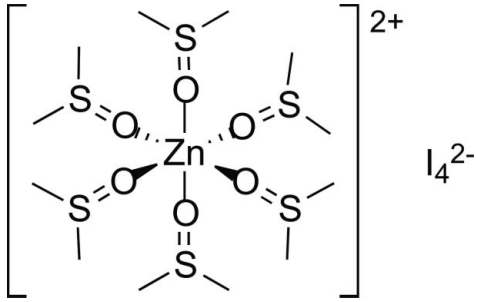
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(S–C) = 0.007 Å; R factor = 0.047; wR factor = 0.104; data-to-parameter ratio = 31.5.

The title compound, $[Zn\{(CH_3)_2SO\}_6]I_4$, is a one-dimensional supramolecular polymer along a threefold rotation axis of the space group. It is built up from discrete $[Zn\{(CH_3)_2SO\}_6]^{2+}$ units connected through non-classical hydrogen bonds to linear I_4^{2-} polyiodide anions (C—H···I = 3.168 Å). The Zn^{II} ion in the cation has an octahedral coordination geometry, with all six Zn—O bond lengths being equivalent, at 2.111 (4) Å. The linear polyiodide anion contains a neutral I_2 molecule weakly coordinated to two iodide ions.

Related literature

For related structures, see Garzón-Tovar *et al.* (2013); Long *et al.* (1999); Tkachev *et al.* (1994). For supramolecular polymers formed by non-classical hydrogen bonds, see: Fromm (2001); Huang & Scherman (2012); Youm *et al.* (2006). For polyiodide compounds, see: Svensson & Kloo (2003).



Experimental

Crystal data

$[Zn(C_2H_6OS)_6]I_4$
M_r = 1041.79
Trigonal, $R\overline{3}$
a = 11.8399 (7) Å
c = 19.7110 (12) Å
V = 2393.0 (2) Å^3
Z = 3
Mo $K\alpha$ radiation
μ = 5.06 mm^{-1}
T = 298 K
0.60 × 0.40 × 0.40 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.126, T_{max} = 0.132
3127 measured reflections
1512 independent reflections
1251 reflections with > 2.0$\sigma(I)$
R_{int} = 0.036

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.104
S = 1.17
1512 reflections
48 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.00 e Å^{-3}
$\Delta\rho_{min}$ = −1.23 e Å^{-3}

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL97* and *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2643).

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S1. Comment

Supramolecular polymers are defined as polymeric systems that extend beyond the molecule by a process of self-assembly between monomer units directed by noncovalent interactions (Huang & Scherman, 2012). These noncovalent forces, such as hydrogen bonding, coordination bonds, π–π stacking and electrostatic forces act as driving forces to construct a well defined supramolecular architectures (Fromm, 2001); however, there are a few examples where non-classical hydrogen bonds such as C—H···I are used to construct these structures (Youm *et al.*, 2006). Previous studies have suggested that a coordination complex with DMSO such as $[Cu(DMSO)_6]^{2+}$ acts as monomeric units connected through a self-assembly process with tetraiodide ions driven by weak non-classical hydrogen bonds C—H···I to form a one-dimensional supramolecular polymer (Garzón-Tovar *et al.*, 2013). Herein we report the synthesis and structural characterization of a new supramolecular polymer.

In the title compound, $[Zn\{(CH_3)_2SO\}_6]I_4$, the Zn(II) ion is located on a 3-fold inversion axis being coordinated by six equidistant oxygen-bonded dimethyl sulfoxide ligands (Fig. 1). The Zn—O bond distances in the $[Zn(DMSO)_6]^{2+}$ complex are 2.111 (4) Å and 87.28 (16), 92.71 (16) ° bond angles. The linear tetraiodide chain presents a neutral I—I molecule with bond distance of 2.8417 (18) Å, weakly coordinated with two iodide (I^-) anions (bond distance 3.335 (1) Å). This result is in agreement with other studies, where the I_4^{2-} correspond to interaction of two I^- anions with one I_2 molecule ($I^{\delta-}$(I—I)$I^{\delta-}$) (Long *et al.*,1999). The two end-iodide anions build up three weak hydrogen bonds to the hydrogen atoms of the methyl groups with distances of 3.167 Å (Fig. 2) to form a one-dimensional supramolecular polymer.

S2. Experimental

Zinc (II) chloride (1.1404 g, 8.3659 mmol) was added to a DMSO (16.506 g, 211.26 mmol) and distilled water (0.199 g, 11.1 mmol) solution. After colorless mixture was ultrasonicated for 20 min, CH_3I (3.420 g, 24.09 mmol) was added, and ultrasonication was continued for an additional 20 min. The resulting yellow solution was kept at 20°C for 8 d, with continuous agitation. The mixture was filtered, and the filtrate was refrigerated at 4°C for 30 d, after which blue crystals with a metallic luster formed. The crystals of $[Zn\{(CH_3)_2SO\}_6]I_4$ were filtered and dried under vacuum. The yield obtained was 0.3231 g.

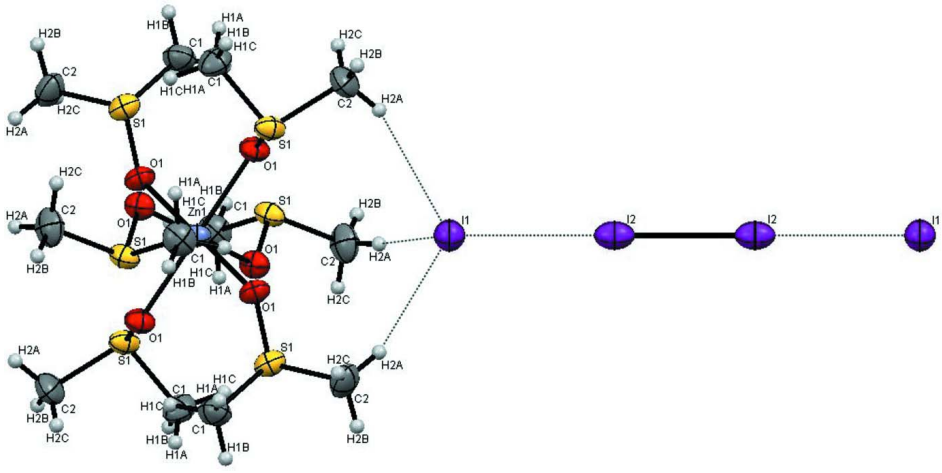

Figure 1

Molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level. H atoms represented by small spheres of arbitrary radii.

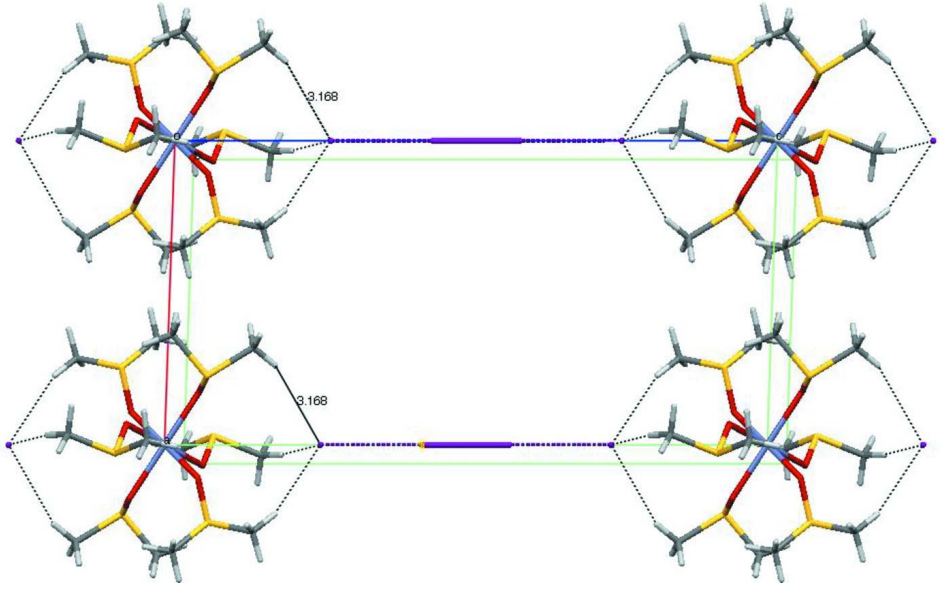

Figure 2

The crystal packing of the title compound viewed along the *b* axis. The C—H···I hydrogen bonds are shown as dashed lines.

Hexakis(dimethyl sulfoxide-κO)zinc(II) polyiodide

Crystal data

$[Zn(C_2H_6OS)_6]I_4$
$M_r = 1041.79$
Trigonal, $R\overline{3}$
Hall symbol: -R 3
$a = 11.8399\ (7)$ Å
$c = 19.7110\ (12)$ Å
$V = 2393.0\ (2)$ Å^3
$Z = 3$
$F(000) = 1482$
$D_x = 2.169$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3127 reflections
$\theta = 3$–30°
$\mu = 5.06$ mm^{-1}

T = 298 K
Plate, 1orange

0.60 × 0.40 × 0.40 mm

Data collection

Nonius KappaCCD diffractometer
Graphite 002 monochromator
ω scans
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.126, T_{max} = 0.132
3127 measured reflections

1512 independent reflections
1251 reflections with > 2.0σ(I)
R_{int} = 0.036
θ_{max} = 30.0°, θ_{min} = 2.9°
h = 0→16
k = −14→0
l = −27→27

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.104
S = 1.17
1512 reflections
48 parameters
0 restraints
H-atom parameters constrained

$1/[\sigma^2(F_o^2) + (0.P)^2 + 55.1589P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.00 e Å^{-3}
$\Delta\rho_{min}$ = −1.23 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008)
Extinction coefficient: 0.30E-02

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. Outlier data were removed using a local program based on the method of Prince and Nicholson. Refinement on F^2 for ALL reflections except for 0 with very negative F^2 or flagged by the user for potential systematic errors. Weighted R-factors wR and all goodnesses 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 observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating R_factor_obs *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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
I1	0.6667	0.3333	0.59206 (4)	0.0430 (3)
I2	0.0000	0.0000	0.42791 (5)	0.0466 (3)
Zn1	0.6667	0.3333	0.3333	0.0258 (3)
S1	0.62508 (13)	0.54407 (13)	0.40794 (8)	0.0316 (3)
O1	0.7243 (4)	0.5025 (4)	0.3922 (2)	0.0324 (9)
C1	0.6592 (7)	0.6747 (6)	0.3515 (4)	0.0423 (15)
C2	0.6825 (8)	0.6355 (7)	0.4845 (3)	0.0478 (16)
H1A	0.7491	0.7411	0.3559	0.063*
H1B	0.6045	0.7105	0.3625	0.063*
H1C	0.6425	0.6428	0.3057	0.063*
H2A	0.6836	0.5804	0.5199	0.072*
H2B	0.6256	0.6680	0.4972	0.072*
H2C	0.7691	0.7074	0.4776	0.072*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.0445 (3)	0.0445 (3)	0.0400 (4)	0.02223 (15)	0.0000	0.0000
I2	0.0356 (3)	0.0356 (3)	0.0688 (6)	0.01778 (14)	0.0000	0.0000
Zn1	0.0221 (4)	0.0221 (4)	0.0331 (8)	0.0111 (2)	0.0000	0.0000
S1	0.0264 (6)	0.0250 (6)	0.0409 (8)	0.0110 (5)	0.0057 (5)	−0.0013 (5)
O1	0.033 (2)	0.0274 (18)	0.040 (2)	0.0174 (16)	0.0017 (17)	−0.0037 (16)
C1	0.049 (4)	0.038 (3)	0.049 (4)	0.028 (3)	0.005 (3)	0.008 (3)
C2	0.066 (5)	0.044 (4)	0.037 (3)	0.030 (4)	0.003 (3)	−0.009 (3)

Geometric parameters (Å, º)

I2—I2^{i}	2.8417 (18)	S1—C1	1.780 (6)
Zn1—O1^{ii}	2.111 (4)	S1—C2	1.782 (7)
Zn1—O1^{iii}	2.111 (4)	C1—H1A	0.9600
Zn1—O1^{iv}	2.111 (4)	C1—H1B	0.9600
Zn1—O1	2.111 (4)	C1—H1C	0.9600
Zn1—O1^{v}	2.111 (4)	C2—H2A	0.9600
Zn1—O1^{vi}	2.111 (4)	C2—H2B	0.9600
S1—O1	1.515 (4)	C2—H2C	0.9600
O1^{ii}—Zn1—O1^{iii}	179.9980 (10)	O1—S1—C2	104.4 (3)
O1^{ii}—Zn1—O1^{iv}	87.29 (16)	C1—S1—C2	98.6 (3)
O1^{iii}—Zn1—O1^{iv}	92.71 (16)	S1—O1—Zn1	119.0 (2)
O1^{ii}—Zn1—O1	87.29 (16)	S1—C1—H1A	109.50
O1^{iii}—Zn1—O1	92.71 (16)	S1—C1—H1B	109.50
O1^{iv}—Zn1—O1	92.71 (16)	H1A—C1—H1B	109.50
O1^{ii}—Zn1—O1^{v}	92.71 (16)	S1—C1—H1C	109.50
O1^{iii}—Zn1—O1^{v}	87.29 (16)	H1A—C1—H1C	109.50
O1^{iv}—Zn1—O1^{v}	179.9980 (10)	H1B—C1—H1C	109.50
O1—Zn1—O1^{v}	87.29 (16)	S1—C2—H2A	109.50
O1^{ii}—Zn1—O1^{vi}	92.71 (16)	S1—C2—H2B	109.50
O1^{iii}—Zn1—O1^{vi}	87.29 (16)	H2A—C2—H2B	109.50
O1^{iv}—Zn1—O1^{vi}	87.29 (16)	S1—C2—H2C	109.50
O1—Zn1—O1^{vi}	180.00	H2A—C2—H2C	109.50
O1^{v}—Zn1—O1^{vi}	92.71 (15)	H2B—C2—H2C	109.50
O1—S1—C1	106.1 (3)		
C1—S1—O1—Zn1	−101.8 (3)	O1^{iv}—Zn1—O1—S1	−48.4 (3)
C2—S1—O1—Zn1	154.6 (3)	O1^{v}—Zn1—O1—S1	131.6 (3)
O1^{ii}—Zn1—O1—S1	38.74 (19)	O1^{vi}—Zn1—O1—S1	112 (10)
O1^{iii}—Zn1—O1—S1	−141.26 (19)		

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