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## Polysulfonylamines. CXIV.† *trans*-Di-methyltetrakis(urea-*O*)tin(IV) bis[di-(methanesulfonyl)amidate] acetonitrile monosolvate

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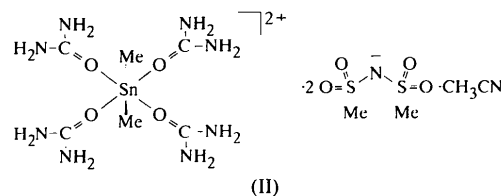
### Abstract

The title complex,  $[\text{Sn}(\text{CH}_3)_2(\text{CH}_4\text{N}_2\text{O})_4](\text{C}_2\text{H}_6\text{NO}_4\text{-S}_2)_2 \cdot \text{C}_2\text{H}_3\text{N}$ , was prepared from  $\text{Me}_2\text{SnBr}_2$ ,  $\text{AgN}(\text{SO}_2\text{Me})_2$  and urea *via* a one-pot reaction in MeCN solution. The asymmetric unit consists of two half cations (of which the Sn atoms lie on inversion centres), two anions and one molecule of acetonitrile. These species are linked into a three-dimensional hydrogen-bonding network, with 15 independent hydrogen bonds formed by amide-H atoms either to the sulfonyl-O atoms of the anions or to the acetonitrile-N atom. The *trans*-octahedral cations exhibit remarkably short Sn—O bonds [2.225 (2)–2.241 (2) Å] and nearly ideal *cis* angles (range  $90 \pm 2.6^\circ$ ). The paddle-wheel conformations of the cations are reinforced by intramolecular N—H...O hydrogen bonds between adjacent urea ligands.

### Comment

In our laboratories, disulfonylamidate species have been successfully employed as non-coordinating counter-ions for unusual organotin(IV) complexes, *e.g.* the elusive aqua complex *trans*- $[\text{Me}_2\text{Sn}(\text{H}_2\text{O})_4]^{2+}$  (Hippel *et al.*, 1993) or the stereochemically dissimilar bis-chelates *trans*- $[\text{Me}_2\text{Sn}(\text{dppoe})_2]^{2+}$  (Wirth *et al.*, 1999) and *cis*- $[\text{Me}_2\text{Sn}(\text{phen})_2]^{2+}$  (Wirth, 1998). Recently, the first structurally authenticated  $[\text{R}_2\text{Sn}(\text{L})_4]^{2+}$  dication featuring a urea-type ligand *L* was observed as the guest entity in the accidentally discovered urea inclusion compound *trans*- $[\text{Me}_2\text{Sn}(\text{ur})_4]^{2+} \cdot 2\text{A}^- \cdot 6(\text{ur})$ , (I), where  $\text{ur} = \text{OC}(\text{NH}_2)_2$  and  $\text{A}^- = (\text{MeSO}_2)_2\text{N}^-$  (Wirth, Moers *et al.*, 1998). In the present contribution, we report the preparation (see *Experimental*) and the crystal structure of the title complex, (II), which is the (solvated) substrate of the inclusion compound (I) and is both chemically and geometrically related to the known analogues *trans*- $[\text{Me}_2\text{Sn}(\text{L})_4]^{2+} \cdot 2\text{A}^-$ , where  $\text{L} = \text{Me}_2\text{SO}$  (Blaschette *et*

*al.*, 1992) or pyridine-1-oxide (Wirth, Blaschette *et al.*, 1998).



The asymmetric unit of (II), as defined by the atomic labelling in Fig. 1, contains two discrete half cations, two non-coordinating anions and one molecule of acetonitrile.

Both *trans*-octahedral  $[\text{Me}_2\text{Sn}(\text{ur})_4]^{2+}$  cations contain an Sn atom on an inversion centre; they closely resemble the single  $C_i$  symmetric cation in (I). Owing to the electron deficiency at the dipositive tin centres, the Sn—O bond lengths, 2.225 (2)–2.241 (2) Å, are remarkably

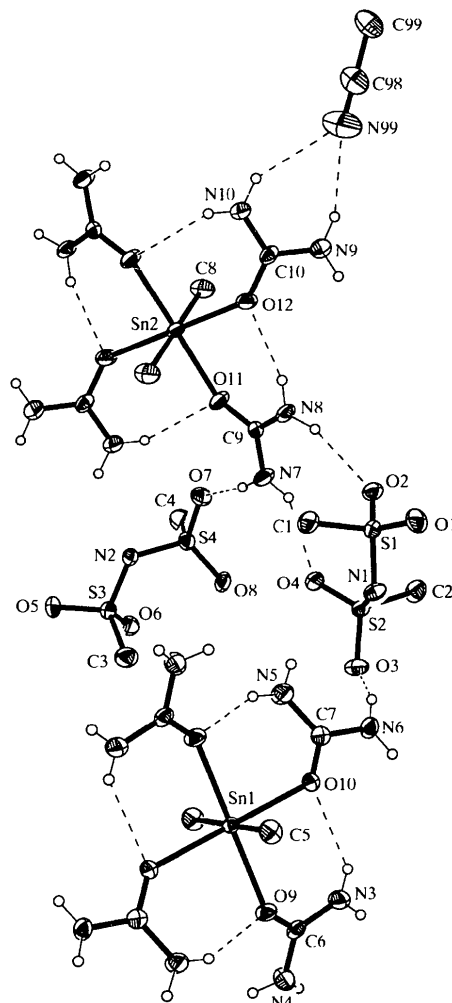


Fig. 1. The structure of the title compound in the crystal. Ellipsoids represent 50% probability levels. Methyl-H atoms have been omitted and H-atom radii are arbitrary. Hydrogen bonds are indicated by dashed lines. Only the asymmetric unit is numbered.

† Part CXIII: Hiemisch *et al.* (1999).

short when compared with the Sn—O distances of 2.40–2.53 Å in the uncharged octahedral complexes [R<sub>2</sub>SnCl<sub>2</sub>(ethyleneurea)<sub>2</sub>] (R = Me: Tavridou *et al.*, 1993; R = Bu: Tavridou *et al.*, 1995); concomitantly, the *cis* angles in (II) do not deviate from 90° by more than ±2.6° (see Table 1). The paddle-wheel conformation of each cation is stabilized by two independent intramolecular hydrogen bonds (N—H···O) formed between adjacent urea ligands (Table 2, first four entries). Whereas the Sn—O—C angles at the donor atoms lie in the narrow range 130.9(2)–134.3(2)°, significantly different orientations relative to the equatorial SnO<sub>4</sub> planes are observed for the N—C—N planes of independent ligands. These variations result from rotations about the Sn—O and O—C bonds and are illustrated first by a selection of torsion angles C—O—Sn—O in Table 1 and secondly by the angles between corresponding Sn—O—C<sub>n</sub> and N—C<sub>n</sub>—N planes [41.8(4), 14.3(6), 18.6(5) and 58.6(3)° for C6, C7, C9 and C10, respectively]. Within the urea molecules, the C—O and C—N distances lie in the ranges 1.258(4)–1.282(4) Å (average 1.270 Å) and 1.314(5)–1.343(4) Å (average 1.326 Å), respectively. The OCN<sub>2</sub> skeletons are essentially planar, the largest observed deviation from coplanarity being 0.011(3) Å for C6.

Both (MeSO<sub>2</sub>)<sub>2</sub>N<sup>−</sup> ions feature bond lengths and bond angles that match those commonly found for ionic di(methanesulfonyl)amidates (see *e.g.* Henschel *et al.*, 1997; Weitze *et al.*, 1995, and references therein), but it can be seen from the O—S—N—S torsion angles in Table 1 that the ions are substantially distorted from the usual approximately C<sub>2</sub> symmetric conformation.

Apart from the intracationic hydrogen bonds mentioned above, an intricate three-dimensional hydrogen-bonding network is present in the crystal, with 15 independent hydrogen bonds (Table 2) formed by amide-H atoms to either the sulfonyl-O atoms of the anions or the acetonitrile-N atom. The intracationic and six of the intermolecular hydrogen bonds are shown in Fig. 1; *cf.* Wirth (1998) for a series of figures illustrating further details of the packing. Obviously the conformational distortions of both the cations and anions (see above) must be attributed to crystal-packing forces arising from the geometric requirements of the hydrogen-bonding network; similar distortions have been observed for the inclusion compound (I), whose structure contains two intracationic and 21 intermolecular hydrogen bonds.

## Experimental

Compound (II) was prepared *via* a one-pot reaction, starting with a solution containing AgN(SO<sub>2</sub>Me)<sub>2</sub> (0.905 g, 3.23 mmol) and urea (0.388 g, 6.46 mmol) in acetonitrile (25 ml), to which was slowly added a solution of Me<sub>2</sub>SnBr<sub>2</sub> (0.500 g, 1.62 mmol) in the same solvent (15 ml). After stirring the mixture for 3 h at 343 K, AgBr was removed by filtration and the hot filtrate cooled slowly to room temperature. One of the

colourless and transparent needles, which had separated after one day, was removed from the mother liquor and without delay subjected to low-temperature structure analysis. When freed from the mother liquor and dried *in vacuo*, the solvate rapidly loses MeCN (elemental analysis unsatisfactory). The effective yield of partially desolvated product was *ca* 50% (0.61 g; m.p. 409 K). <sup>1</sup>H NMR (CD<sub>3</sub>CN, 200 MHz, p.p.m.): δ 0.92 (s, 6H, CH<sub>3</sub>Sn), 2.86 (s, 12H, CH<sub>3</sub>S), 4.5–6.0 (*sbr.*, 16H, NH<sub>2</sub>); <sup>2</sup>J(<sup>119</sup>Sn—H) = 110.4 Hz, <sup>2</sup>J(<sup>117</sup>Sn—H) = 105.8 Hz.

## Crystal data

[Sn(CH<sub>3</sub>)<sub>2</sub>(CH<sub>4</sub>N<sub>2</sub>O)<sub>4</sub>]-  
(C<sub>2</sub>H<sub>6</sub>NO<sub>4</sub>S<sub>2</sub>)<sub>2</sub>·C<sub>2</sub>H<sub>3</sub>N

*M<sub>r</sub>* = 774.46

Monoclinic

C2/c

*a* = 47.600(6) Å

*b* = 6.6063(8) Å

*c* = 22.135(2) Å

β = 116.371(9)°

*V* = 6236.4(12) Å<sup>3</sup>

*Z* = 8

*D<sub>x</sub>* = 1.650 Mg m<sup>−3</sup>

*D<sub>m</sub>* not measured

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 63

reflections

θ = 3.0–12.5°

μ = 1.155 mm<sup>−1</sup>

*T* = 173(2) K

Needle

0.4 × 0.1 × 0.1 mm

Colourless

## Data collection

Siemens P4 diffractometer

ω scans

Absorption correction:

ψ scan (XEMP; Siemens,  
1994a)

*T<sub>min</sub>* = 0.795, *T<sub>max</sub>* = 0.891

5455 measured reflections

5384 independent reflections

4037 reflections with

*I* > 2σ(*I*)

*R<sub>int</sub>* = 0.019

θ<sub>max</sub> = 25°

*h* = −56 → 1

*k* = 0 → 7

*l* = −23 → 23

3 standard reflections

every 247 reflections

intensity decay: none

## Refinement

Refinement on *F*<sup>2</sup>

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.030

*wR*(*F*<sup>2</sup>) = 0.062

*S* = 0.907

5384 reflections

435 parameters

H atoms treated by a

mixture of independent

and constrained refinement

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0274*P*)<sup>2</sup>]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

(Δ/σ)<sub>max</sub> = 0.001

Δρ<sub>max</sub> = 0.36 e Å<sup>−3</sup>

Δρ<sub>min</sub> = −0.50 e Å<sup>−3</sup>

Extinction correction: none

Scattering factors from

*International Tables for  
Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Sn1—C5	2.094 (3)	Sn2—C8	2.201 (4)
Sn1—O9	2.225 (2)	Sn2—O11	2.125 (2)
Sn1—O10	2.239 (2)	Sn2—O12	2.241 (2)
O9—Sn1—O10	90.90 (8)	C8—Sn2—O12	91.35 (13)
C5—Sn1—O9	88.50 (12)	C6—O9—Sn1	133.3 (2)
C5—Sn1—O10	87.64 (12)	C7—O10—Sn1	134.3 (2)
O11—Sn2—O12	92.60 (8)	C9—O11—Sn2	132.0 (2)
C8—Sn2—O11	88.81 (12)	C10—O12—Sn2	130.9 (2)
O10—Sn1—O9—C6	−38.5 (3)	O3—S2—N1—S1	−169.0 (2)
O9—Sn1—O10—C7	−34.1 (3)	O4—S2—N1—S1	−42.4 (3)
O12—Sn2—O11—C9	30.8 (3)	O5—S3—N2—S4	−158.31 (19)
O11—Sn2—O12—C10	−47.6 (3)	O6—S3—N2—S4	−30.0 (3)
O1—S1—N1—S2	−146.0 (2)	O7—S4—N2—S3	−168.08 (19)
O2—S1—N1—S2	−16.9 (3)	O8—S4—N2—S3	−40.2 (3)

Symmetry codes: (i) 1 − *x*, −1 − *y*, 1 − *z*; (ii)  $\frac{1}{2}$  − *x*,  $\frac{1}{2}$  − *y*, 1 − *z*.

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

D—H...A	D—H	H...A	D...A	D—H...A
N3—H01...O10	0.839 (16)	2.36 (3)	3.083 (4)	144 (3)
N5—H05...O9 <sup>i</sup>	0.839 (16)	2.20 (2)	2.971 (4)	153 (3)
N8—H012...O12	0.833 (16)	2.159 (19)	2.963 (4)	162 (4)
N10—H016...O11 <sup>ii</sup>	0.842 (16)	2.49 (3)	3.062 (4)	126 (3)
N3—H01...O11 <sup>iii</sup>	0.839 (16)	2.50 (3)	2.957 (4)	115 (3)
N3—H02...O6 <sup>iv</sup>	0.840 (16)	2.19 (2)	2.980 (4)	157 (3)
N4—H03...O8 <sup>v</sup>	0.831 (16)	2.118 (19)	2.924 (4)	163 (3)
N4—H04...O4 <sup>v</sup>	0.828 (15)	2.186 (18)	2.992 (4)	165 (3)
N6—H07...O3	0.850 (15)	2.25 (2)	2.996 (4)	146 (3)
N6—H08...O11 <sup>iii</sup>	0.831 (15)	2.220 (17)	3.047 (4)	173 (3)
N7—H09...O7	0.836 (15)	2.066 (19)	2.881 (4)	165 (4)
N7—H010...O4	0.840 (16)	2.23 (3)	2.970 (4)	147 (4)
N8—H011...O2	0.838 (15)	2.109 (19)	2.909 (4)	160 (3)
N8—H011...O5 <sup>vi</sup>	0.838 (15)	2.60 (3)	2.864 (4)	100 (3)
N8—H012...O5 <sup>vi</sup>	0.833 (16)	2.60 (4)	2.864 (4)	100 (3)
N9—H013...N99	0.836 (16)	2.22 (2)	3.024 (5)	160 (4)
N9—H014...O5 <sup>vi</sup>	0.834 (16)	2.123 (18)	2.944 (4)	168 (4)
N10—H015...N99	0.851 (15)	2.63 (3)	3.328 (6)	140 (3)
N10—H016...O7 <sup>ii</sup>	0.842 (16)	2.34 (3)	2.970 (4)	132 (3)

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

NH were freely refined but with N—H bond lengths restrained as equal (command *SADI*; Sheldrick, 1997); methyl-H atoms were located from difference syntheses, idealized and refined as rigid groups allowed to rotate, but not tip.

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *XP* (Siemens, 1994b). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1351). Services for accessing these data are described at the back of the journal.

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## [2-(2-Pyridyl-N)quinoxaline-N<sup>1</sup>]silver(I) nitrate

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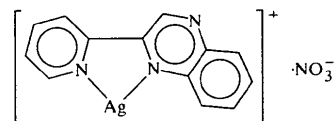
(Received 24 May 1999; accepted 19 August 1999)

## Abstract

The title compound, [Ag(C<sub>13</sub>H<sub>9</sub>N<sub>3</sub>)]NO<sub>3</sub>, is an infinite one-dimensional polymer. Each Ag atom is coordinated by three N atoms, with Ag—N bond distances in the range of 2.246 (3)–2.413 (3) Å.

## Comment

Much effort has been devoted recently to the design of metal complexes exhibiting helical or polymeric architectures which have particular relevance to biological systems and asymmetric catalysis. Several silver(I) polymer helices have been reported (Tong *et al.*, 1998; Hester *et al.*, 1997; Carlucci *et al.*, 1998; Psillakis *et al.*, 1997). In this paper, we report the crystal structure of a silver(I)–2-(2-pyridyl)quinoxaline complex, (I).



(I)

Each Ag atom is, as expected in a three-coordinate environment, linked to three N atoms from two different 2-(2-pyridyl)quinoxaline molecules, resulting in trigonal coordination distorted toward Y-shaped geometry [N3—Ag1—N2( $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ )] 141.2 (1)°, N1—