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Complexes of dimethyltin dihalides with *N*-methylpyrrolidinone, $C_{12}H_{24}N_2O_2X_2Sn$ (X = Cl, Br or I)

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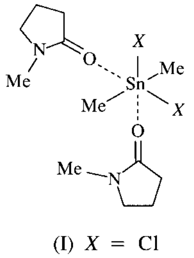
The single-crystal X-ray structure determinations of the title complexes, *cis*-dichloro-*trans*-dimethyl-*cis*-bis(*N*-methylpyrrolidin-2-one-*O*)tin(IV), $[Sn(CH_3)_2Cl_2(C_5H_9NO)_2]$, *cis*-dibromo-*trans*-dimethyl-*cis*-bis(*N*-methylpyrrolidin-2-one-*O*)tin(IV), $[SnBr_2(CH_3)_2(C_5H_9NO)_2]$, and *cis*-diiodo-*trans*-dimethyl-*cis*-bis(*N*-methylpyrrolidin-2-one-*O*)tin(IV), $[Sn(CH_3)_2I_2(C_5H_9NO)_2]$, show that those tin complexes in which coordination of the lactam ligand to Sn^{IV} is realized *via* oxygen exhibit a distorted octahedral geometry.

Comment

Molecular complexes of dimethyltin dihalides with electron-donor solvents such as dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF) have been explored extensively (Tanaka, 1967; Isaacs *et al.*, 1968; Aslanov *et al.*, 1978). Studies of complexes of the related *N*-methylpyrrolidinone (NMP) ligand have not been published to date. The structures of the title complexes, *cis*-dichloro-*trans*-dimethyl-*cis*-bis(*N*-methylpyrrolidin-2-one-*O*)tin(IV), (I), *cis*-dibromo-*trans*-dimethyl-*cis*-bis(*N*-methylpyrrolidin-2-one-*O*)tin(IV), (II), and *cis*-diiodo-*trans*-dimethyl-*cis*-bis(*N*-methylpyrrolidin-2-one-*O*)tin(IV), (III), have been determined as part of our study on the Stille reaction in which the compounds investigated can be



(I) X = Cl
(II) X = Br
(III) X = I

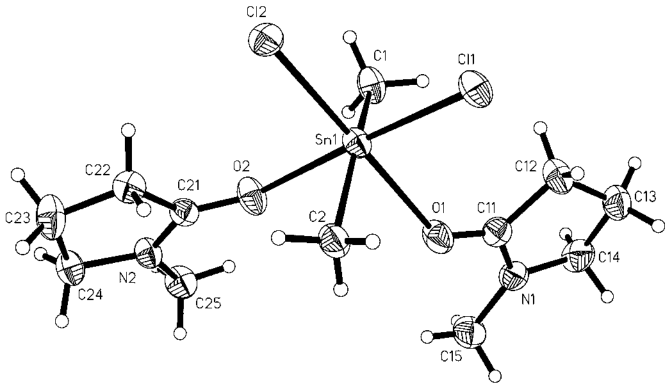


Figure 1
View of compound (I) showing the atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as circles of arbitrary radii.

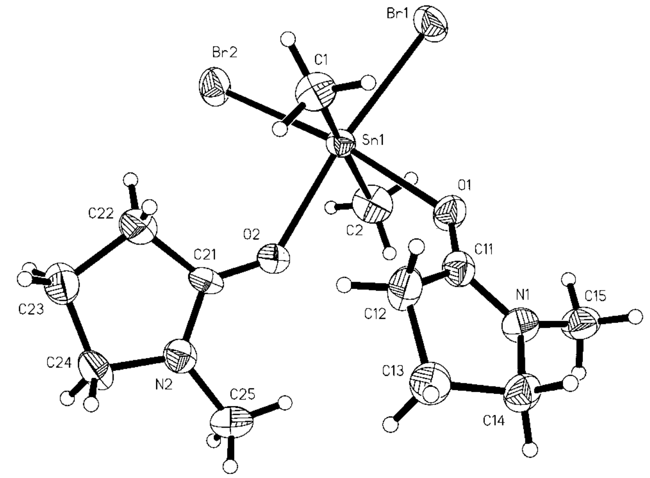


Figure 2
View of compound (II) showing the atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as circles of arbitrary radii.

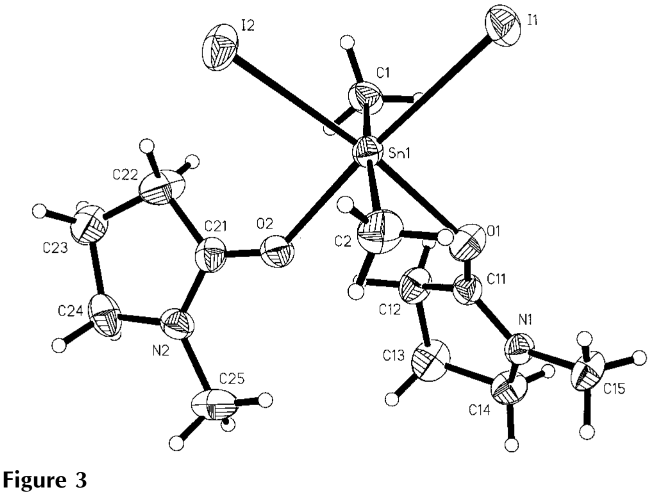


Figure 3
View of compound (III) showing the atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as circles of arbitrary radii.

formed as by-products. These complexes show great promise for studying solvent effects on organometallic reactions.

In all three cases, the crystals exhibit distorted octahedral geometry. The degree of distortion becomes obvious when the angles C—Sn—C and O—Sn—halogen are compared. The values are as follows: (I) C—Sn—C 159.57 (9), O—Sn—Cl 177.76 (4) and 178.02 (4)°; (II) C—Sn—C 169.7 (4), O—Sn—Br 172.17 (15) and 173.67 (15)°; (III) C—Sn—C 170.3 (2), O—Sn—I 173.19 (8) and 175.46 (7)°.

The bond lengths and angles in the NMP ligand of complexes (I)–(III) agree well with those in the uncoordinated ligand (Müller *et al.*, 1996). In the dichloro compound, (I), the torsion angles of both NMP ligands are within the range reported previously. In the dibromo compound, (II), the torsion angle C11—C12—C13—C14 increases to 23.7 (10)°, while in the diiodo compound, (III), the torsion angle C12—C13—C14—N1 is 22.3 (5)°. In these three compounds, the deviation from planarity is larger than in uncomplexed NMP. The orientation of the NMP ligands can be described by the following torsion angles: Sn—O1—C11—N1 −153.53 (18)° in (I), 152.4 (6)° in (II) and −160.0 (3)° in (III); Sn—O2—C21—N2 −165.15 (16)° in (I), 171.3 (6)° in (II) and −177.4 (3)° in (III). These orientations could be determined by the C15—H···O1 and C25—H···O2 interactions with H···O distances in the range 2.41–2.47 Å, C···O distances in the range 2.811 (12)–2.850 (3) Å and C—H···O angles in the range 103–104°.

There are only slight differences between the bond lengths in the Sn—C fragment [2.105 (2) and 2.111 (2) Å in (I), 2.098 (8) and 2.114 (9) Å in (II), and 2.109 (4) and 2.119 (4) Å in (III)] and they are comparable with reported values (Skinner & Sutton, 1944; Fujii & Kimura, 1971; Aslanov *et al.*, 1978). The Sn–halogen bonds are longer [2.4737 (7) and 2.4768 (8) Å in (I), 2.6738 (10) and 2.6761 (12) Å in (II), and 2.9135 (7) and 2.9299 (7) Å in (III)] than in the uncomplexed compounds and correlate with the values for related organotin complexes with DMF or DMSO (Isaacs & Kennard, 1970; Aslanov *et al.*, 1978).

A comparative study of the values of the Sn—O bond lengths leads to the unexpected result that the Sn—O bonds in the dichloro compound are the longest in the series [2.4464 (16) and 2.4598 (15) Å] and are thus a little longer than in the related DMF compound (2.390 Å; Aslanov *et al.*, 1978). In the dibromo [2.323 (6) and 2.345 (6) Å] and the diiodo [2.294 (3) and 2.326 (3) Å] compounds, the Sn—O bond lengths are almost the same. This can be explained by the tendency of Cl to react as an electron acceptor. In the trinuclear, almost linear, fragment O_{NMP}—Sn—Cl, the Cl can draw out of the Sn—O bond the electron density delivered by O. Consequently, the Sn—Cl bond becomes shorter and the Sn—O bond length increases (Aslanov *et al.*, 1978). This effect might well be expected to be even greater on going from Br to I, but the size of the ligand in fact seems to become predominant.

In (II) and (III), there are no intermolecular interactions exceeding van der Waals distances, whereas in (I), weak C—H···Cl interactions are also effective.

Experimental

All three compounds were prepared by a similar route. Freshly sublimed dichlorodimethylstannane (2.20 g, 10 mmol), derived from the reaction of dimethyltin oxide with HCl (Pfeiffer, 1902) or dibromodimethylstannane (3.09 g, 10 mmol) was mixed in an atmosphere of argon with a solution of *N*-methylpyrrolidinone (1.98 g, 20 mmol) in dry diethyl ether (10 ml). After stirring for 30 min, the mixture was stored in a refrigerator at 278 K. Colourless crystals were obtained in quantitative yield for the dichloro compound, (I) (m.p. 318 K). The structure-relevant NMR parameters are $^2J(^{119}\text{Sn}—\text{C}—^1\text{H})$, $^1J(^{119}\text{Sn}—^{13}\text{C})$ and $\delta(^{119}\text{Sn})$. A solution of the complex (70 mg) in C_6D_6 (420 mg) gave values of 86 Hz, 678 Hz and −47.5 p.p.m., respectively. These values represent an equilibrium which was, as expected, shifted when a solution of the complex (40 mg) in NMP (590 mg) was studied: $^2J(^{119}\text{Sn}—\text{C}—^1\text{H})$ = 104 Hz, $^1J(^{119}\text{Sn}—^{13}\text{C})$ = 865 Hz and $\delta(^{119}\text{Sn})$ = −154.6 p.p.m. Colourless crystals were obtained in quantitative yield for the dibromo compound, (II) (m.p. 315 K). A solution of the complex (80 mg) in C_6D_6 (410 mg) gave the following values for the structure-relevant NMR parameters: $^2J(^{119}\text{Sn}—\text{C}—^1\text{H})$ = 84 Hz, $^1J(^{119}\text{Sn}—^{13}\text{C})$ = 636 Hz and $\delta(^{119}\text{Sn})$ −94.0 p.p.m. The following values were measured for the complex (40 mg) dissolved in NMP (410 mg): $^2J(^{119}\text{Sn}—\text{C}—^1\text{H})$ = 105 Hz, $^1J(^{119}\text{Sn}—^{13}\text{C})$ = 863 Hz and $\delta(^{119}\text{Sn})$ = −204.5 p.p.m. Diiododimethylstannane was obtained according to the literature method of Armitage & Tarassoli (1975) by a halide-exchange reaction of dichlorodimethylstannane with trimethyliodosilane and finally distilled *in vacuo* before use. Following the described experimental route, yellow crystals of (III) were obtained in quantitative yield (m.p. 326 K). A solution of the complex (80 mg) in C_6D_6 (410 mg) gave the following values for the structure-relevant NMR parameters: $^2J(^{119}\text{Sn}—\text{C}—^1\text{H})$ = 71 Hz, $^1J(^{119}\text{Sn}—^{13}\text{C})$ = 462 Hz and $\delta(^{119}\text{Sn})$ = −197.9 p.p.m. The following values were obtained for the complex (60 mg) dissolved in NMP (370 mg): $^2J(^{119}\text{Sn}—\text{C}—^1\text{H})$ = 103 Hz, $^1J(^{119}\text{Sn}—^{13}\text{C})$ = 854 Hz and $\delta(^{119}\text{Sn})$ = −284.8 p.p.m. Crystals for the diffraction experiments were obtained by slow evaporation of solutions of the title compounds in diethyl ether.

Compound (I)

Crystal data

$[Sn(CH_3)_2Cl_2(C_5H_9NO)_2]$
M_r = 417.92
Monoclinic, $P2_1/c$
a = 7.8320 (16) Å
b = 25.703 (5) Å
c = 8.9840 (18) Å
β = 111.38 (3)°
V = 1684.0 (6) Å^3
Z = 4

D_x = 1.648 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6276 reflections
θ = 2.56–25.67°
μ = 1.834 mm^{-1}
T = 173 (2) K
Parallelepiped, colourless
0.15 × 0.10 × 0.10 mm

Table 1
Hydrogen-bonding geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C12—H12*B*···Cl1^{i}	0.97	2.90	3.662 (3)	139
C14—H14*B*···Cl1^{ii}	0.97	2.82	3.698 (3)	152
C24—H24*B*···Cl2^{iii}	0.97	2.99	3.916 (3)	159
C22—H22*B*···Cl2^{iv}	0.97	2.82	3.742 (3)	158

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

Data collection

Nonius KappaCCD diffractometer
935 frames *via* ω-rotation ($\Delta\omega = 1^\circ$) at different θ values and 2×20 s per frame
6276 measured reflections
3188 independent reflections
2598 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.019$
$\theta_{\rm max} = 25.67^\circ$
$h = -9 \rightarrow 9$
$k = -31 \rightarrow 31$
$l = -10 \rightarrow 10$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.050$
$S = 0.984$
3188 reflections
176 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0286P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.005$
$\Delta\rho_{\rm max} = 0.317$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.589$ e Å^{-3}

Compound (**II**)

Crystal data

$[{\rm SnBr_2(CH_3)_2(C_5H_9NO)_2}]$
$M_r = 506.84$
Monoclinic, *Pn*
$a = 7.4750$ (15) Å
$b = 8.0300$ (16) Å
$c = 14.977$ (3) Å
$\beta = 91.98$ (3)°
$V = 898.4$ (3) Å^3
$Z = 2$

$D_x = 1.874$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3025 reflections
$\theta = 2.54$–25.67°
$\mu = 5.870$ mm^{-1}
$T = 173$ (2) K
Parallelepiped, colourless
$0.1 \times 0.1 \times 0.1$ mm

Data collection

Nonius KappaCCD diffractometer
265 frames *via* ω-rotation ($\Delta\omega = 1^\circ$) at different θ values and 2×60 s per frame
3025 measured reflections
1711 independent reflections (plus 1308 Friedel-related reflections)

2893 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.005$
$\theta_{\rm max} = 25.67^\circ$
$h = -9 \rightarrow 8$
$k = -9 \rightarrow 9$
$l = -18 \rightarrow 18$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.104$
$S = 1.115$
3019 reflections
177 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0588P)^2 + 2.0195P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.892$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.850$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0055 (14)
Absolute structure: Flack (1983)
Flack parameter = 0.370 (13)

Compound (**III**)

Crystal data

$[{\rm Sn(CH_3)_2I_2(C_5H_9NO)_2}]$
$M_r = 600.82$
Monoclinic, *Pn*
$a = 7.3960$ (10) Å
$b = 8.327$ (2) Å
$c = 15.406$ (3) Å
$\beta = 90.31$ (3)°
$V = 948.8$ (3) Å^3
$Z = 2$

$D_x = 2.103$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7279 reflections
$\theta = 2.45$–27.12°
$\mu = 4.601$ mm^{-1}
$T = 173$ (2) K
Parallelepiped, pale yellow
$0.07 \times 0.07 \times 0.05$ mm

Data collection

Nonius KappaCCD diffractometer
652 frames *via* ω-rotation ($\Delta\omega = 1^\circ$) at different θ values and 2×50 s per frame
7279 measured reflections
2108 independent reflections)plus 1836 Friedel-related reflections)

3469 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.026$
$\theta_{\rm max} = 27.12^\circ$
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -19 \rightarrow 18$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.043$
$S = 0.946$
3944 reflections
176 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0075P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.542$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.583$ e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = −0.01 (2)

All H atoms were placed in calculated positions and refined with a riding model (including free rotation about C—C bonds), with $U_{\rm iso}$ constrained to be $1.5U_{\rm eq}$ of the carrier atom. The absolute structure of the bromine derivative, (II), could not be determined reliably [Flack (1983) parameter 0.366 (13), $R1 = 0.0382$ and $wR2 = 0.1036$]. The inverse of the configuration presented in this paper resulted in poorer residuals [Flack parameter 0.466 (15), $R1 = 0.0400$ and $wR2 = 0.1093$] and was therefore rejected. The data were not corrected for absorption and a possible absorption effect for the bromine derivative, (II), which is the strongest absorber of the three compounds, cannot be excluded.

For all compounds, data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL*97 and *PARST*95 (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1448). Services for accessing these data are described at the back of the journal.

References

Armitage, D. A. & Tarassoli, A. (1975). *Inorg. Chem.* **14**, 1210–1211.
Aslanov, L. A., Ionov, V. M., Attiya, V. M., Permin, A. B. & Petrosyan, V. S. (1978). *J. Struct. Chem.* **19**, 91–98.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Fujii, H. & Kimura, M. (1971). *Bull. Chem. Soc. Jpn*, **44**, 2643–2647.
Isaacs, N. W. & Kennard, C. H. L. (1970). *J. Chem. Soc. A*, pp. 1257–1261.
Isaacs, N. W., Kennard, C. H. L. & Kitching, W. (1968). *Chem. Commun.* pp. 820–821.
Müller, G., Lutz, M. & Harder, S. (1996). *Acta Cryst.* B**52**, 1014–1022.
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
Nonius (1997). *KappaCCD Server Software*. Windows 3.11 Version. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.
Pfeiffer, P. (1902). *Chem. Ber.* **35**, 3303–3307.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1991). *SHELXTL-Plus.* Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Skinner, H. A. & Sutton, L. E. (1944). *Trans. Faraday Soc.* **40**, 164–184.
Tanaka, T. (1967). *Inorg. Chim. Acta*, **1**, 217–221.