

Acta Crystallographica Section C

**Crystal Structure  
Communications**

ISSN 0108-2701

---

**Bromodimethyl(*N*-methylpyrrolidin-2-one-*O*)tin(IV)-di- $\mu$ -bromo-bromodimethyl-  
tin(IV)**

**Uwe-Christoph König *et al.***

---

**Electronic paper**

This paper is published electronically. It meets the data-validation criteria for publication in Acta Crystallographica Section C. The submission has been checked by a Section C Co-editor though the text in the 'Comments' section is the responsibility of the authors.

© 2000 International Union of Crystallography • Printed in Great Britain – all rights reserved

## Bromodimethyl(*N*-methylpyrrolidin-2-one-*O*)tin(IV)-di- $\mu$ -bromo-bromodimethyltin(IV)

Uwe-Christoph König, Michael Berkei, Claudia Hirsch, Hans Preut\* and Terence Nigel Mitchell

Fachbereich Chemie, Universität Dortmund, Otto-Hahn-Straße 6, 44221 Dortmund, Germany

Correspondence e-mail: uch002@uxp1.hrz.uni-dortmund.de

Received 25 September 2000

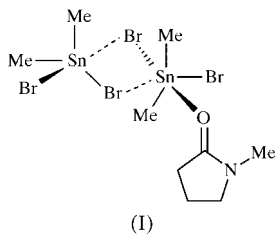
Accepted 23 October 2000

Data validation number: IUC0000303

The preparation and X-ray analysis of the title compound,  $[\text{Sn}_2\text{Br}_4(\text{CH}_3)_4(\text{C}_5\text{H}_9\text{NO})]$ , are described. The compound contains two Sn atoms in the asymmetric unit, that complexed by *N*-methylpyrrolidin-2-one being hexacoordinated (*a*), the other exhibiting pentacoordination (*b*). The most important features are three different Sn—Br bond lengths at both Sn atoms with the following values: (*a*) 2.5060 (9), 2.7152 (10) and 3.7118 (10) Å; (*b*) 2.5084 (10), 2.5279 (9) and 3.5841 (10) Å.

### Comment

Molecular complexes derived from 1:1 and 1:2 complexation of dimethyltin dihalides by *N*-methylpyrrolidinone (NMP) are well known (König *et al.*, 2000*a,b*). The 2:1 complexation of dimethyltin dichloride by NMP shows pentacoordination at both Sn atoms, which are bridged by a chloro ligand, the angle Sn—Cl—Sn being 135.56 (5)°. The values of the Sn—Cl bond lengths are 2.5704 (13) and 3.1159 (13) Å (König, Berkei, Hirsch *et al.*, 2000). Two bridging bromine ligands are found in the analogous adduct of dimethyltin dibromide and NMP, (I). The central atom which is complexed by NMP exhibits the octahedral geometry typically found in hexacoordinated tin complexes, whereas the other Sn atom is surrounded by five ligands, generating a trigonal-bipyramidal geometry.



It is sometimes difficult to pinpoint the geometry around the central atom in certain molecular complexes. The most important parameters measured are the bond angles and bond

lengths. For this reason a definition and quantitative limitation of the term bond can be made satisfactorily with the method of van der Waals radii. This term is used correctly when the measured distance between two atoms is smaller than the sum of the corresponding radii (Bondi, 1964) as for instance between Sn and Br atoms, the sum of whose van der Waals radii is calculated as 4.0–4.2 Å.

The Sn—C bond lengths of the pentacoordinated tin centre have normal values of 2.095 (5) and 2.126 (5) Å (Ho & Zuckerman, 1973). The deviation from ideal geometry in the equatorial plane is smaller than in other pentacoordinated complexes of dimethyltin dihalides and NMP (König *et al.*, 2000*b*; König, Berkei, Hirsch *et al.*, 2000), as is demonstrated most clearly by the values of the angles C1—Sn1—C2, C1—Sn1—Br1 and C2—Sn1—Br1: 132.4 (3), 106.98 (15) and 107.75 (14)°. The bromine ligands Br2 and Br4 take apical positions, the values of the Sn—Br bond lengths and the angle Br2—Sn1—Br4 being as follows: 2.5279 (9), 3.5841 (10) Å and 177.99 (3)°. The variation from the trigonal-bipyramidal geometry becomes most obvious from an extraordinarily small difference between the apical and equatorial bromine positions. The Sn1—Br1 bond has a length of 2.5084 (10) Å and is therefore only little shorter than the Sn1—Br2 bond.

The ligands in the equatorial plane are somewhat displaced towards the bridging bromine ligand Br4. This becomes evident from the values of the angles between the axial and the equatorial ligands: (*a*) Br2—Sn1—C1 102.38 (14)°, Br2—Sn1—C2 103.82 (15)°, Br2—Sn1—Br1 98.17 (3)°; (*b*) Br4—Sn1—C1 79.14 (14)°, Br4—Sn1—C2 74.17 (15)°, Br4—Sn1—Br1 82.57 (3)°.

Another difference between the chlorine and bromine derivatives lies in the angles Sn1—X4—Sn2 (*X* = Cl, Br). In the latter complex this angle has a value of 99.29 (3)° and thus is approximately 36° smaller than in the chlorine complex. The value of the second bridging angle Sn1—Br1—Sn2 is 100.17 (3)°.

At the hexacoordinated tin, the values of the Sn—C bond lengths are 2.107 (6) Å and 2.116 (7) Å and thus lie in the normal range. The angle C3—Sn2—C4 (138.3(3)°) is obviously smaller than the analogous angle 169.7 (4)° at the hexacoordinated central atom in *cis*-dibromo-*trans*-dimethyl-*cis*-bis(*N*-methylpyrrolidinone)tin(IV) (König *et al.*, 2000*a*).

The Sn—Br bonds in the hexacoordinated part of the complex differ greatly and can be regarded as the adducts most interesting feature. The Sn2—Br4 bond has a value of 2.7152 (10) Å and is thus because of the bridging character of Br4 a little longer [2.6738 (10) and 2.6761 (12) Å] than in a related hexacoordinated complex (König *et al.*, 2000*a*). The angle Br4—Sn2—O1 is almost linear [175.82 (14)°]. Nevertheless, the bond between the bromine ligand Br3 and Sn2 has a length of 2.5060 (9) Å which is typical of a Sn—Br bond in the equatorial plane of a trigonal bipyramid (Boer *et al.*, 1970; König *et al.*, 2000*b*). This is confirmed by the angles C3—Sn2—C4, C3—Sn2—Br3 and C4—Sn2—Br3 having the following values: 138.3 (3), 111.2 (2) and 109.48 (19)°.

As in *cis*-dibromo-*trans*-dimethyl-*cis*-bis(*N*-methylpyrrolidinone)tin(IV) (König *et al.*, 2000*b*) the plane defined by

the two methyl groups and the bromine ligand Br3 is displaced towards the NMP ligand. This becomes evident from the values of the following angles: (a) C3—Sn2—O1 90.1 (2)°, C4—Sn2—O1 83.2 (3)°, Br3—Sn2—O1 87.09 (12)°; (b) C3—Sn2—Br4 94.1 (2)°, C4—Sn2—Br4 93.2 (2)°, Br3—Sn2—Br4 92.11 (3)°.

The deviation from ideal geometry is closely related to the angles involving the bridging bromine ligand Br1: Br1—Sn2—C3 70.2 (2)°, Br1—Sn2—C4 71.44 (19)°, Br1—Sn2—O1 103.18 (12)°, Br1—Sn2—Br3 169.69 (3)°. The fragment C5—O1—Sn2 is not as often expected linear. The angle C5—O1—Sn2 has a value of 139.9 (5)° and is therefore within the range of known values (König, 2000). The value of the Sn2—O1 bond length is 2.271 (5) Å and thus shorter than those in related adducts (König *et al.*, 2000*a,b*).

The values of the bond lengths and bond angles in the NMP ligand are comparable with those observed in other NMP coordinated organometallic compounds (Churchill & Rotella, 1979) and in free NMP (Müller *et al.*, 1996).

### Experimental

The title compound is prepared by the reaction of *N*-methylpyrrolidinone (0.71 g, 0.69 ml, 7.3 mmol) with freshly sublimed dibromodimethylstannane (4.51 g, 14.6 mmol) derived from the reaction of dimethyltin oxide with HBr (Pfeiffer, 1902) in 10 ml of dry diethyl ether. The reaction mixture is stirred for 30 min and afterwards stored in a refrigerator at 278 K. Colourless crystals are obtained in quantitative yield after filtration and drying *in vacuo* (m.p. 320 K). A solution of the complex (40 mg) in C<sub>6</sub>D<sub>6</sub> (430 mg) gives the following values for the structure-relevant NMR parameters: <sup>2</sup>*J*(<sup>119</sup>Sn, <sup>1</sup>H) = 71 Hz, <sup>1</sup>*J*(<sup>119</sup>Sn—<sup>13</sup>C) = 506 Hz and δ(<sup>119</sup>Sn) = 11.6 p.p.m.

#### Crystal data

[Sn<sub>2</sub>Br<sub>4</sub>(CH<sub>3</sub>)<sub>4</sub>(C<sub>5</sub>H<sub>9</sub>NO)]  
*M<sub>r</sub>* = 716.29  
 Orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>  
*a* = 7.5279 (3) Å  
*b* = 10.4817 (4) Å  
*c* = 24.7865 (11) Å  
*V* = 1955.78 (14) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 2.433 Mg m<sup>-3</sup>

Mo *K*α radiation  
 Cell parameters from 12688 reflections  
 θ = 1.64–25.69°  
 μ = 10.715 mm<sup>-1</sup>  
*T* = 173 (2) K  
 Parallelepiped, colourless  
 0.11 × 0.10 × 0.10 mm

#### Data collection

Nonius KappaCCD diffractometer  
 443 frames *via* ω-rotation (Δω = 1°)  
 at different κ angles and two times 75 s per frame  
 12 688 measured reflections  
 3713 independent reflections

2662 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.073  
 θ<sub>max</sub> = 25.69°  
*h* = -9 → 8  
*k* = -12 → 12  
*l* = -29 → 30

#### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.036  
*wR*(*F*<sup>2</sup>) = 0.065  
*S* = 0.903  
 3713 reflections  
 154 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0131P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 (Δ/σ)<sub>max</sub> = 0.001  
 Δρ<sub>max</sub> = 0.78 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.98 e Å<sup>-3</sup>  
 Absolute structure: Flack (1983);  
 1570 Friedel pairs  
 Flack parameter = 0.117 (10)

**Table 1**

Selected geometric parameters (Å, °).

Sn1—C1	2.095 (5)	Sn2—C4	2.116 (7)
Sn1—C2	2.126 (5)	Sn2—O1	2.271 (5)
Sn1—Br1	2.5084 (10)	Sn2—Br3	2.5060 (9)
Sn1—Br2	2.5279 (9)	Sn2—Br4	2.7152 (10)
Sn1—Br4	3.5841 (10)	Sn2—Br1	3.7118 (10)
Sn2—C3	2.107 (6)		
C1—Sn1—C2	132.4 (3)	C4—Sn2—Br3	109.48 (19)
C1—Sn1—Br1	106.98 (15)	O1—Sn2—Br3	87.09 (12)
C2—Sn1—Br1	107.75 (14)	C3—Sn2—Br4	94.1 (2)
C1—Sn1—Br2	102.38 (14)	C4—Sn2—Br4	93.2 (2)
C2—Sn1—Br2	103.82 (15)	O1—Sn2—Br4	175.82 (14)
Br1—Sn1—Br2	98.17 (3)	Br3—Sn2—Br4	92.11 (3)
C1—Sn1—Br4	79.14 (14)	C3—Sn2—Br1	70.2 (2)
C2—Sn1—Br4	74.17 (15)	C4—Sn2—Br1	71.44 (19)
Br1—Sn1—Br4	82.57 (3)	O1—Sn2—Br1	103.18 (12)
Br2—Sn1—Br4	177.99 (3)	Br3—Sn2—Br1	169.69 (3)
C3—Sn2—C4	138.3 (3)	Br4—Sn2—Br1	77.58 (2)
C3—Sn2—O1	90.1 (2)	Sn1—Br1—Sn2	100.17 (3)
C4—Sn2—O1	83.2 (3)	Sn2—Br4—Sn1	99.29 (3)
C3—Sn2—Br3	111.2 (2)		

The data collection covered almost the whole sphere of reciprocal space. The crystal-to-detector distance was 35 mm. Crystal decay was monitored by repeating the initial frames at the end of data collection. Analysing the duplicate reflections there was no indication for any decay. H atoms were placed in calculated positions with *U*<sub>iso</sub> constrained to be 1.2*U*<sub>eq</sub> of the carrier atom.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *SHELXL97* and *PARST95* (Nardelli, 1995).

### References

- Boer, F. P., Doorakian, G. A., Freedman, H. H. & McKinley, S. V. (1970). *J. Am. Chem. Soc.* **92**, 1225–1233.  
 Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.  
 Churchill, M. R. & Rotella, F. J. (1979). *Inorg. Chem.* **18**, 853–860.  
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.  
 Ho, B. Y. K. & Zuckerman, J. J. (1973). *J. Organomet. Chem.* **49**, 1–84.  
 König, U.-C. (2000). Doctoral Thesis, University of Dortmund, Germany.  
 König, U.-C., Berkei, M., Hirsch, C., Preut, H. & Mitchell, T. N. (2000). *Acta Cryst.* **C56**, e450–451.  
 König, U.-C., Berkei, M., Neikes, F., Preut, H. & Mitchell, T. N. (2000*a*). *Acta Cryst.* **C56**, e53–e54.  
 König, U.-C., Berkei, M., Neikes, F., Preut, H. & Mitchell, T. N. (2000*b*). *Acta Cryst.* **C56**, 324–326.  
 Müller, G., Lutz, M. & Harder S. (1996). *Acta Cryst.* **B52**, 1014–1022.  
 Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.  
 Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.  
 Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter & R. M. Sweet, pp. 307–326. London: Academic Press.  
 Pfeiffer, P. (1902). *Chem. Ber.* **35**, 3303–3307.  
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.  
 Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.