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Short Communication

# Crystal and molecular structure of potassium 18-crown-6-[2,6-bis(dimethylaminomethyl)phenyl]tin(IV) tetrafluoride

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## Abstract

The crystal structure of the title compound shows the [K(18-crown-6)]$^+$ cation and [{2,6-($Me_2NCH_2$)$_2$$C_6H_3$}$SnF_4$]$^-$ anion, which are held together through two potassium-fluorine and one potassium-tin electrostatic interaction. The tin atom is hexacoordinated by one carbon and four fluorine atoms, and an intramolecular N→Sn interaction. It has a distorted octahedral configuration. Electrostatic interactions between two fluorine atoms and hydrogen atoms from two different cation–anion pairs generate a double-chain polymeric supramolecular structure, containing both isomers.

**Keywords:** crown ether; hydrogen bond; hypercoordination; organotin fluoride.

## Introduction

Among the organotin fluorides containing intramolecularly coordinating ligands reported so far (Pieper et al., 1997; Altmann et al., 2000; Varga et al., 2006; Novák et al., 2007; Švec and Růžička, 2011), to the best of our knowledge there is only one monoorganotin(IV) fluoride (Novák et al., 2007). We report here on the crystal and molecular structure of the title compound [K(18-crown-6)]$^+$[{2,6-($Me_2NCH_2$)$_2$$C_6H_3$}$SnF_4$]$^-$.

The unit cell of potassium 18-crown-6-*N,C,N*-[2,6-bis(dimethylaminomethyl)phenyl]tin(IV) tetrafluoride, [K(18-crown-6)]$^+$[{2,6-($Me_2NCH_2$)$_2$$C_6H_3$}$SnF_4$]$^-$ contains the cation and the anion, which are connected by potassium–fluorine electrostatic interactions at K(1)-F(3) and K(1)-F(4) distances of 2.578(2) and 2.636(2) Å, respectively. These and the Sn(1)-K(1) [3.612(1) Å] distances are all shorter than the sum of the van der Waals radii for the corresponding atoms [$\Sigma_{vdW}$(K,F) ≈ 4.2 Å, $\Sigma_{vdW}$(K,Sn) ≈ 4.9 Å] (Emsley, 1994).

The Sn(1) atom is hexa-coordinated by C(1), F(1)-F(4) and N(1) and shows a distorted octahedral configuration (Figure 1). The distortion of the octahedral geometry at the tin atom is indicated by the deviation of the C(1)-Sn(1)-F(4) [161.62(14)°], N(1)-Sn(1)-F(2) [172.63(12)°], and F(1)-Sn(1)-F(3) [170.01(10)°] angles from the ideal value of 180° (Table 1).

The four Sn-F distances are slightly different and fall in the narrow range between 1.960(2) Å [Sn(1)-F(2)] and 2.001(2) Å [Sn(1)-F(3)] (Table 1). These distances compare well with those reported for:

- [{2,6-($Me_2NH^+CH_2$)$_2$$C_6H_3$}$SnF_4^-$] [Sn(1)-F(1) 1.9522(14) Å;
- Sn(1)-F(2) 1.9613(14) Å; Sn(1)-F(3) 2.0302(13) Å;
- Sn(1)-F(4) 1.9835(14) Å] (Novák et al., 2007), [2,6-($Me_2NCH_2$)$_2$$C_6H_3$]$_2$$SnF_2$ [Sn(1)-F(1) 1.988(2) Å;
- Sn(1)-F(2) 1.984(2) Å] (Rotar et al., 2008), [{$Me_2N(CH_2)_3$}$_2$$SnF_2$]·2$H_2O$ [2.084(6) Å] (Pieper et al., 1997);
- [2-($Me_2NCH_2$)$_2$$C_6H_4$]$_2$$SnF_2$ [Sn(1)-F(1) 1.9726(14) Å; and
- Sn(1)-F(2) 1.9774(13) Å) (Varga et al., 2006).

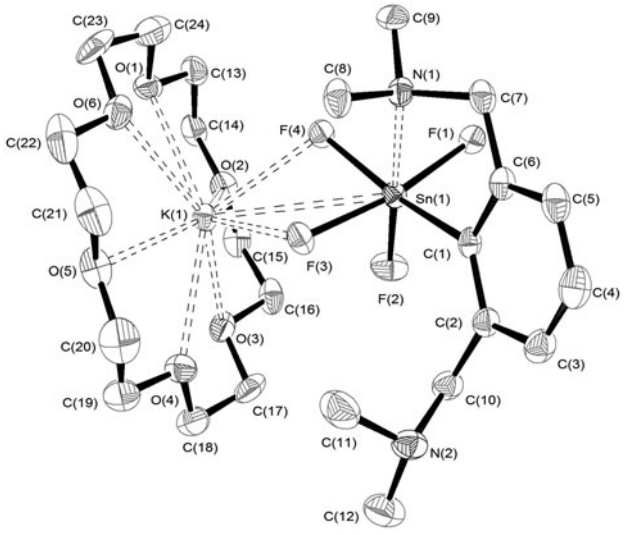


**Figure 1** ORTEP representation at 30% probability and atom numbering scheme of the isomer (*R*)-[K(18-crown-6)]$^+$[{2,6-($Me_2NCH_2$)$_2$$C_6H_3$}$SnF_4$]$^-$. Hydrogen atoms have been omitted for clarity.

**Table 1** Selected interatomic distances (Å) and angles (degrees) in $[K(18\text{-crown-6})]^+[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}SnF_4]^-$.

| | | | |
|---|---|---|---|
| Sn(1)-F(1) | 1.987 (2) | K(1)-O(3) | 2.966 (6) |
| Sn(1)-(2) | 1.960 (2) | K(1)-O(4) | 2.831 (6) |
| Sn(1)-F(3) | 2.001 (2) | K(1)-O(5) | 2.953 (6) |
| Sn(1)-F(4) | 1.972 (2) | K(1)-O(6) | 2.836 (5) |
| Sn(1)-N(1) | 2.320 (3) | | |
| Sn(1)-C(1) | 2.164 (4) | C(1)-Sn(1) - F(4) | 161.62 (14) |
| Sn(1)-K(1) | 3.612 (10) | F(1)-Sn(1) - F(3) | 170.01 (10) |
| K(1)-F(3) | 2.578 (2) | F(2)-Sn(1) - N(1) | 172.63 (12) |
| K(1)-F(4) | 2.636 (2) | | |
| K(1)-O(1) | 2.975 (8) | | |
| K(1)-O(2) | 2.820 (15) | | |

The tin-nitrogen distance of 2.320(3) Å is comparable to those found in compounds $[\{2,6\text{-}(Me_2NH^+CH_2)_2C_6H_3\}SnF_4^-]$ [2.325(2) Å] (Novák et al., 2007) and $[\{Me_2N(CH_2)_3\}_2SnF_2]\cdot 2H_2O$ [2.366(8) Å] (Pieper et al., 1997). It is shorter than the corresponding bonds in $[2\text{-}(Me_2NCH_2)_2C_6H_4]_2SnF_2$ [2.5083(18) and 2.6064(18) Å] (Varga et al., 2006) and $[2,6\text{-}(Me_2NCH_2)_2\text{-}C_6H_3]_2SnF_2$ [2.576(2) and 2.470(2) Å] (Rotar et al., 2008).

The intramolecular N(1)→Sn(1) coordination induces planar chirality at the tin atom (Opris et al., 2003, 2004; Bumbu et al., 2004; Kulcsar et al., 2005; Varga et al., 2005, 2006) and the compound reported here crystallized as a racemate.

Due to the above-mentioned interactions, the potassium atom is displaced in the direction of the Sn(1) atom out of the plane of the oxygen atoms from the crown ether. This builds the equatorial plane of a hexagonal pyramid.

In addition to intramolecular F(2)···$H(10A)_{methylene\text{-}N}$ (2.483 Å), F(3)···$H(8C)_{methyl}$ (2.342 Å), F(3)···$H(11A)_{methyl}$ (2.448 Å) and F(4)···$H(9A)_{methyl}$ (2.267 Å) interactions being shorter than the sum of the van der Waals radii of the corresponding atoms [cf. $\Sigma_{vdW}$(F,H) 2.55 Å] (Emsley, 1994), see Figure 2, the intermolecular fluorine–hydrogen interactions result in a double-chain polymeric structure, see Figure 3. The supramolecular structure contains dimers of (*R*) and (*S*) isomers [F(4)···$H(14B')_{methylene\text{-}crown}$ 2.330 Å], which are further associated through weaker F···H [F(1)···$H(22Ba)_{methylene\text{-}crown}$ 2.510(2) Å] interactions.

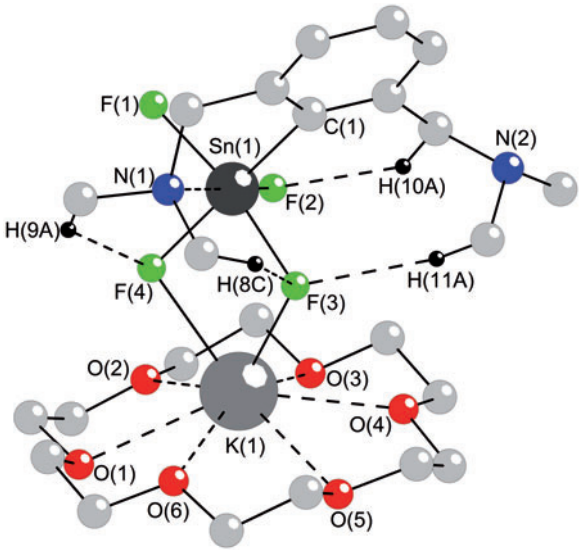


**Figure 2** View of the intramolecular hydrogen bonding system (only the hydrogen atoms involved in intramolecular interactions are shown) in the $[K(18\text{-crown-6})]^+[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}\text{-}SnF_4]^-$ crystal.

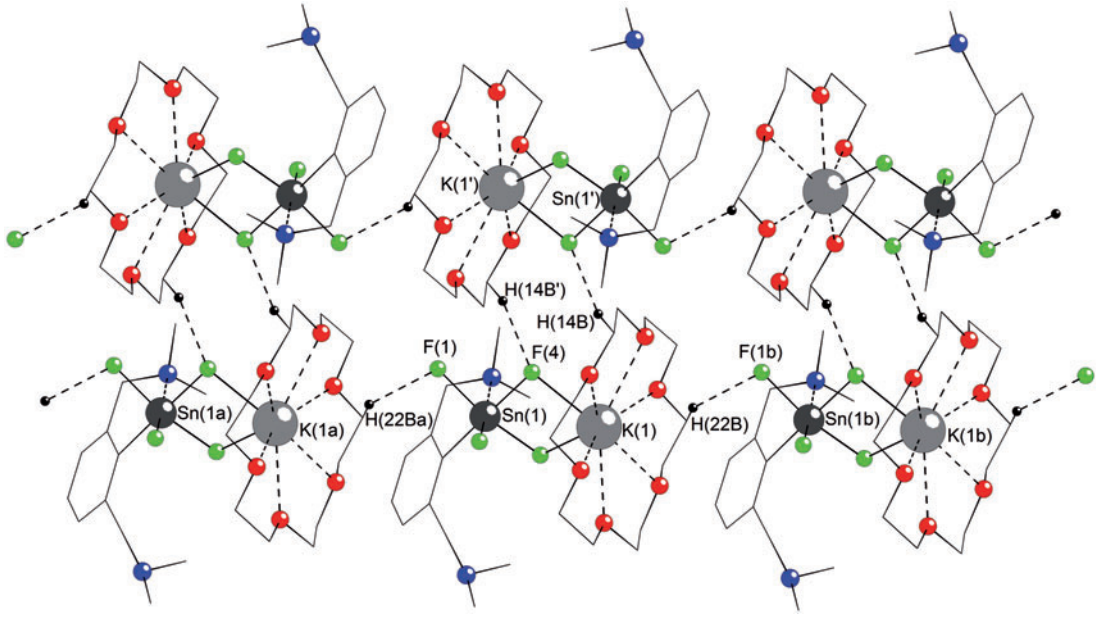


**Figure 3** View of the supramolecular ribbon-like association based on intermolecular hydrogen bonding (only hydrogen atoms involved in intermolecular interactions are shown) in the $[K(18\text{-crown-6})]^+[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}SnF_4]^-$ crystal [symmetry equivalent atoms (*1-x, 1-y, 1-z*), (*x, 1+y, z*) and (*x,-1+ y, z*) are given by 'prime', 'a' and 'b'].

## Experimental part

[18-crown-6] (0.29 g, 1.104 mmol) and excess KF was added to a solution of $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]SnCl_3$ (0.46 g, 1.104 mmol) in 45 ml anhydrous $CH_2Cl_2$. The reaction mixture was stirred for 18 h and then filtered to remove the resulting KCl. The clear filtrate was evaporated *in vacuo* and the residue was re-crystallized from $CH_2Cl_2$/*n*-hexane (approx. 1:4) to give $[K(18\text{-crown-}6)]^+[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}SnF_4]^-$ (0.5 g, 65.78%) as colorless crystals (mp 78–79°C). $^1$H nuclear magnetic resonance or NMR ($CDCl_3$, 300.1 MHz, 20°C): $\delta$ 2.42 (s, 12H, $NCH_3$), 2.54 (s, 4H, $CH_2N$), 3.60 (s, 24H, $(CH_2)_{12}O_6$), 7.24–7.37 (complex pattern, $C_6H_5$). $^{13}$C NMR ($CD_2Cl_2$, 75.4 MHz, 20°C): $\delta$ 40.9 (s, $NCH_3$), 45.4 (s, $CH_2N$), 70.1 [s, $(CH_2)_{12}O_6$], 127.1 (s, $C_m$), 128.40 (s, $C_p$), 141.92 (s, $C_o$). $^{19}$F NMR ($CD_2Cl_2$, 282.4 MHz, 20°C): $\delta$-147.6 (s, $^1J(^{19}F\text{-}^{119}Sn)$=2302 Hz). $^{119}$Sn ($CDCl_3$, 111.9 MHz, 20°C). No resonance was observed at room temperature.

Intensity data for the colorless $[K(18\text{-crown-}6)]^+[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}SnF_4]^-$ crystal were collected on a Nonius KappaCCD diffractometer (Universität Dortmund) with graphite-monochromated MoKa radiation at 150 K. Cell constants are given in Table 2, along with other experimental parameters and relevant information about the structure solution and refinement.

The structures were solved by direct methods (Sheldrick, 1990). Refinement applied the full-matrix least-squares methods (Sheldrick, 1997). Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from *International Tables for X-ray Crystallography* (Wilson, 1992). All of the non-hydrogen atoms were treated anisotropically. Figures were created using the ORTEP 3 program produced by Chemical Crystallography, Glasgow, UK (Farrugia, 1997) and the Diamond program produced by Crystal Impact GbR, Germany (Brandenburg, 1996).

CCDC-855048 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

**Table 2** Crystal data and structure refinement for $[K(18\text{-crown-}6)]^+[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}SnF_4]^-$.

| | |
|---|---|
| Empirical formula | $C_{24}H_{43}F_4KN_2O_6Sn$ |
| Formula weight | 689.39 |
| Temperature (K) | 293(2) |
| Wavelength (Å) | 0.71073 |
| Crystal system | Monoclinic |
| Space group | *P2(1)/c* |
| Unit cell dimensions | |
| *a* (Å) | 18.9550 (10) |
| *b* (Å) | 10.1470 (10) |
| *c* (Å) | 16.1830 (10) |
| $\beta$ (°) | 101.570 (10) |
| Volume (Å$^3$) | 3049.3 (4) |
| *Z* | 4 |
| $D_c$ (g/cm$^3$) | 1.502 |
| Absorption coefficient (mm$^{-1}$) | 1.037 |
| *F(000)* | 1416 |
| Crystal size (mm) | 0.1×0.1×0.2 |
| θ range for data collections (°) | 2.97–27.47 |
| Reflections collected | 6941 |
| Independent reflections | 6941 [R(int)=0.00] |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 6941/0/280 |
| Goodness-of-fit on $F^2$ | 0.883 |
| Final *R* indices [$I>2\sigma(I)$] | $R_1$=0.0468, $wR_2$=0.0996 |
| *R* indices (all data) | $R_1$=0.0994, $wR_2$=0.1076 |
| Largest diff. peak and hole, eA$^{-3}$ | 1.071 and -0.683 |

## Acknowledgments

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