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X-ray Structure Analysis Online

Crystal Structure of 4-Nitroanilinium Tetrachlorodimethylstannate(IV)

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The structure of a new organotin(IV) complex with formula $[4\text{-}NH_3C_6H_4\text{–}NO_2]^+{}_2[Sn(CH_3)_2Cl_4]^{2-}$ is reported. This crystal belongs to space group $P2_1/c$ with cell dimensions a = 7.8026(4)Å, b = 20.8627(11)Å, c = 6.8990(4)Å, β = 111.4560(10)°; the final R value is 0.0291. This compound exists as a three-dimensional polymer produced by intermolecular N–H···Cl and N–H···O hydrogen bonds. Also, weak C–H···O and C–H···Cl hydrogen bonds were observed in the crystal lattice.

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Organotin(IV) derivatives have been extensively studied as wood preservatives and agrochemical fungicides.[1] The property of organotin compounds, R_2SnX_2 (X = halogen), as Lewis acids has been utilized to prepare trihalodiorganostannates,[2] $[R_2SnX_3]^-$ and tetrahalodiorganostannates,[3] $[R_2SnX_4]^{2-}$. Here, we report on the crystal structure of new complex, 4-nitroanilinium tetrachlorodimethylstannate(IV), $[4\text{-}NH_3C_6H_4\text{–}NO_2]^+{}_2[Sn(CH_3)_2Cl_4]^{2-}$ (Fig. 1). Single crystals of this compound were obtained from a solution of methanol and chloroform in a ratio of 6:1 after slow evaporation at room temperature. The crystal and experimental data are given in Table 1. The structure was solved by direct methods. The positions of the hydrogen atoms were obtained from a difference Fourier map. The atomic coordinates for non-hydrogen atoms are listed in Table 2. Selected bond lengths and angles are given in Table 3.

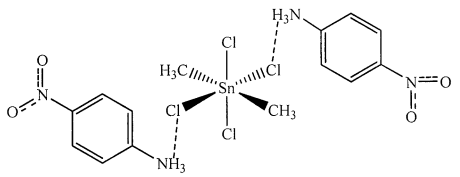

Fig. 1 Chemical structure.

Table 1 Crystal data and structure refinement for the title compound[a]

Formula: $C_{14}H_{20}Cl_4N_4O_4Sn$	
Formula weight = 568.83	Crystal size: 0.3 × 0.2 × 0.14
Crystal system: monoclinic	Temperature: 120(2)
Space group: $P2_1/c$	Z = 2
a = 7.8026(4)Å	β = 111.4560(10)°
b = 20.8627(11)Å	
c = 6.8990(4)Å	
V = 1045.21(10)Å^3	
D_x = 1.807 Mg/m^3	
No. of reflections used = 2772	
$2\theta_{max}$ = 58.0 with Mo K_α	
R = 0.0291 [2628 refs. I>2σ(I)]	
$(\Delta/\sigma)_{max}$ = 0.001	
$(\Delta\rho)_{max}$ = 0.843 eÅ^{-3}	
$(\Delta\rho)_{min}$ = –0.697 eÅ^{-3}	
Measurement: Bruker SMART 1000 CCD	
Program system: SADABS	
Structure determination: SHELXL-97	
Refinement: full-matrix least-squares on F^2	

[a]this compound was deposited to the Cambridge Data Center with the CCDC NO. 259183

Table 2 Fractional coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) of non-hydrogen atoms

Atom	$x \times 10^4$	$y \times 10^4$	$z \times 10^4$	U(eq) × 10^3
Sn(1)	15000	10000	-5000	13(1)
Cl(1)	14078(1)	8797(1)	-5134(1)	22(1)
Cl(2)	13122(1)	10157(1)	-8973(1)	17(1)
C(1SN)	12575(3)	10242(1)	-4476(3)	20(1)
O(1)	7439(2)	6740(1)	-2856(3)	24(1)
O(2)	6070(2)	7541(1)	-2063(3)	24(1)
N(1)	7413(2)	7297(1)	-2264(3)	17(1)
N(2)	13822(2)	8791(1)	-550(3)	17(1)
C(1)	9086(3)	7682(1)	-1803(3)	14(1)
C(2)	10720(3)	7372(1)	-1562(3)	15(1)
C(3)	12292(3)	7742(1)	-1118(3)	15(1)
C(4)	12171(3)	8400(1)	-939(3)	14(1)
C(5)	10528(3)	8708(1)	-1187(4)	18(1)
C(6)	8948(3)	8341(1)	-1623(4)	18(1)

U(eq) = (1/3)$\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* (\boldsymbol{a}_i \cdot \boldsymbol{a}_j)$.

Table 3 Selected bond lengths (Å) and angles (deg) for the title compound

Sn(1)-C(1SN)	2.113(2)	O(1)-N(1)	1.233(3)
Sn(1)-Cl(1)	2.6043(5)	O(1)-N(2)	1.218(2)
Sn(1)-Cl(2)	2.6135(5)	N(1)-C(1)	1.465(3)
C(1SN)#1-Sn(1)-Cl(1)	90.97(7)	Cl(1)#1-Sn(1)-Cl(2)	87.584(17)
C(1SN)-Sn(1)-Cl(1)	89.03(7)	O(2)-N(1)-O(1)	123.41(19)
C(1SN)#1-Sn(1)-Cl(2)	92.53(6)	O(2)-N(1)-C(1)	118.75(18)
C(1SN)-Sn(1)-Cl(2)	87.47(6)	O(1)-N(1)-C(1)	117.85(18)
Cl(1)-Sn(1)-Cl(2)	92.416(17)		

#1 –x+3, –y+2, –z–1

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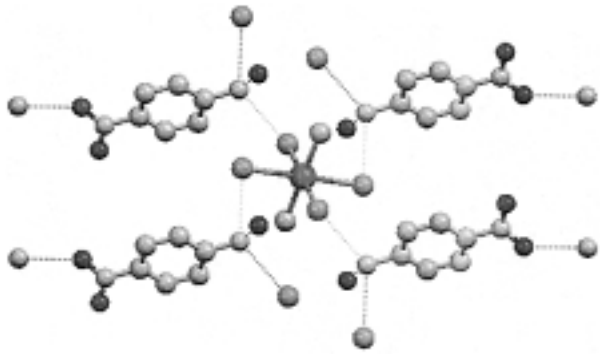

Fig. 2 Intermolecular Cl···H–N hydrogen bonds in title compound showing that each $Sn(CH_3)_2Cl_4^{2-}$ anion is surrounded by four 4-nitroanilinium cations.

The Sn(1)–Cl(1) and Sn(1)–Cl(2) bond lengths are 2.6043(5)Å and 2.6135(5)Å, respectively, lying in the range of the normal covalent radii, 2.37 – 2.60Å.[4] The Sn–C bond lengths, 2.113(2)Å, are quite close to those previously reported in the literature.[5] The title compound exists as a three-dimensional polymer produced by intermolecular hydrogen bonds. Each $Sn(CH_3)_2Cl_4^{2-}$ anion is connected to four 4-nitroanilinium cations by N(2)–H(2NA)···Cl(1) and N(2)–H(2NC)···Cl(2) hydrogen bonds (Fig. 2 and Table 4). The N(2)–H(2NB)···O(1) intermolecular hydrogen bond (Table 4) is formed between NO_2 and NH_3^+ moieties of two neighboring cations. In the crystal lattice, there are two weak C–H···O hydrogen bonds, [C(3)–H(3A)···O(2) with 3.291 Å and ∠C(3)–H(3A)···O(2) = 119.60˚], [C(3)–H(3A)···O(2) with 3.270 Å and ∠C(3)–H(3A)···O(2) = 145.14˚]. Also, there are four weak C–H···Cl hydrogen bonds such that the two of them form between the H(2A) and H(3A) atoms and the Cl(1) atom of one anion, [C(2)–H(2A)···Cl(1) with 3.448 Å and ∠C(2)–H(2A)···Cl(1) = 123.06˚], [C(3)–H(3A)···Cl(1) with 3.466 Å and ∠C(3)–H(3A)···Cl(1) = 122.32˚]. The two other weak C–H···Cl hydrogen bonds form between the H(5A) and H(6A) atoms and Cl(2) atoms of two different neighboring anions, [C(5)–H(5A)···Cl(2) with 3.649 Å and ∠C(5)–H(5A)···Cl(2) = 135.59˚], [C(6)–H(6A)···Cl(2) with 3.617 Å and ∠C(6)–H(6A)···Cl(2) = 131.40˚]. In this structure, each $Sn(CH_3)_2Cl_4^{2-}$ anion forms a weak C(1SN)–H(1SC)···Cl(2) [with 3.666 Å and ∠C(1SN)–H(1SC)···Cl(2) = 171.08˚] hydrogen bond with neighboring anions.

Table 4 Hydrogen bond D-H··A for the title compound

D-H···A	D-H(Å)	H··A(Å)	D··A(Å)	∠D-H··A(˚)
N(2)-H(2NA)…Cl(1)	0.95	2.30	3.240(3)	170
N(2)-H(2NB)…O(1)^{i}	0.95	2.04	2.967(3)	166
N(2)-H(2NC)…Cl(2)^{ii}	0.95	2.27	3.170(3)	159

Symmetry operations i) *x*+1, –*y*+3/2, *z*+1/2; ii) *x*, *y*, *z*+1

References

1. A. Bacchi, M. Carcelli, P. Pelagatti, G. Pelizzi, M. C. Rodriguez-Arguelles, D. Rogolino, C. Solinas, and F. Zani, *J. Inorg. Biochem*., **2005**, *99*, 397.
2. E. M. Garcia, A. G. Sanchez, A. Castineiras, J. S. Cases, and J. Sordo, *J. Organomet. Chem*., **1994**, *469*, 41.
3. J. Ouyang, Y. Zu, and L. E. Khoo, *J. Organomet. Chem*., **1998**, *561*, 143.
4. F. H. Allen, S. A. Bellard, M. D. Brice, B. A. Cartwright, A. Doubleday, H. Higgs, T. Hummelink, B. G. Hummelink-Peters, O. Kennard, W. D. S. Motherwell, J. R. Rogers, and D. G. Waston, *Acta Crystallogr., Sect. B*, **1979**, *35*, 2331.
5. C. L. Ma, F. Li, Q. Jiang, and R. F. Zhang, *J. Organomet. Chem*., **2004**, *689*, 96.