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Original Scientific Paper

Trigonal-bipyramidal Anion $[Ph_2Cl_3Sn]^-$ in the Structure of *N*-[(Diethylphosphoryl)methyl]-piperidinium Diphenyltrichlorostannate(IV)*

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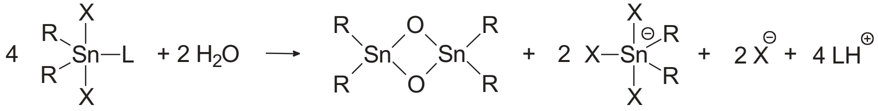
Crystal structure of *N*-[(diethylphosphoryl)methyl]-piperidinium diphenyltrichlorostannate(IV), $[C_{10}H_{23}NO_3P]^+$ $[C_{12}H_{10}Cl_3Sn]^-$ has been determined, $a = 11.416(2)$, $b = 11.582(2)$, $c = 12.491(2)$ Å, $\alpha = 69.82(2)$, $\beta = 81.22(2)$, $\gamma = 60.73(2)°$, space group $P\bar{1}$, 4493 reflections, $R(F) = 0.0271$, $wR(F^2) = 0.0712$. The structure consists of isolated trigonal-bipyramidal anions and hydrogen-bonded dimers formed by cations. The impact of secondary Sn···Cl interactions on the geometry of complex anions is discussed.

Key words: crystal structure, tin(IV), hydrogen bond, hydrolysis.

INTRODUCTION

During our studies on the complexes of organotin halides with phosphoryl ligands,[1] we have found that these complexes are easily hydrolyzed if the ligand contains aliphatic amino group. The tentative scheme of hydrolysis is presented below.



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* Dedicated to Professor Boris Kamenar on the occasion of his 70th birthday.

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Recently, we have briefly reported the crystal structure of the product of such hydrolysis: bis [di(*i*-propyl)phosphoryl]-(dimethylammonium)methane dibutyltrichlorostannate(IV) (**I**).[2] In this work, we present the crystal structure of *N*-[(diethyl-phosphoryl)methyl]-piperidinium diphenyltrichlorostannate(IV) (**II**) arising from the hydrolysis of the complex formed by diphenyltin dichloride and *N*-[(diethylphosphoryl)methyl] piperidine.

EXPERIMENTAL

Dichloromethane solutions of diphenyltin dichloride and *N*-[(diethylphosphoryl)methyl]-piperidine taken in 1 : 2 ratio were mixed and the obtained complex was precipitated by addition of hexane. The crystals were grown from $CHCl_3$ / heptane. A specimen of approximate dimensions 0.15 × 0.25 × 0.30 mm was used with an Enraf-Nonius CAD-4 diffractometer (Mo-Kα radiation, ω scan, $\Theta_{max} = 24.47°$). Of the total 4493 independent reflections recorded, 3945 were with $I > 2\sigma(I)$. Empirical absorption correction using seven ψ-scan curves was applied,[3] $T_{max} = 0.820$, $T_{min} = 0.639$. The structure was solved with SHELXS96[4] and refined with SHELXL93.[5] Ethyl group attached to O(3) is disordered over two sets of sites [atoms C(9) and C(10) with occupations of 0.76(2), and C(91) and C(101) with occupation of 0.24(2)]. All hydrogens, except for those of disordered ethyl group, were located from a difference Fourier map and refined isotropically, all non-H atoms were given anisotropically. The refinement led to $R(F) = 0.0271$ and $wR(F^2) = 0.0712$. Details of structure determination are deposited with the Cambridge Crystallographic Data Centre, deposition number 103119. Final fractional atomic coordinates for all non-H atoms and principal bond lengths and angles are given in Tables I, II.

Crystal Data. $C_{22}H_{33}Cl_3NO_3PSn$, $M_r = 615.50$, triclinic, space group $P\bar{1}$, $a = 11.416(2)$, $b = 11.582(2)$, $c = 12.491(2)$ Å, $\alpha = 69.82(2)$, $\beta = 81.22(2)$, $\gamma = 60.73(2)°$, $V = 1352.0(8)$ Å^3, $Z = 2$, $D_{calc} = 1.512$ g cm^{-3}, $\mu = 1.323$ mm^{-1}.

RESULTS AND DISCUSSION

ORTEP[6] drawings of **II** with the atom labelling scheme and the crystal packing motif are presented in Figures 1 and 2. The tin atoms have a regular trigonal bipyramidal environment and, in contrast to **I**, in structure **II** the secondary contacts Sn $\cdots$ Cl are absent. The cations form hydrogen-bonded centrosymmetric dimers, parameters of this medium-strong hydrogen bond being: O(1) $\cdots$ N 2.782(4) Å, O(1) $\cdots$ H(1) 1.97(3) Å, N–H(1) $\cdots$ O(1) 168(2). Among the structures containing $[R_2SnCl_3]^-$ anions, there are examples of isolated anions as well as of dimers with the coordination environment of the tin atom complemented up to octahedron. Principal geometric parameters of $[R_2SnCl_3]^-$ anions are collected in Table III. Two first items of this table correspond to the structures where the primary and secondary contacts Sn–Cl are equalized, thus the coordination environment of the tin

TABLE I

Fractional atomic coordinates (x, y, $z \times 10^4$) and equivalent thermal parameters ($U_{eq} \times 10^3$ / Å^2) in structure **II**

Atom	x	y	z	U_{eq}
Sn	5935(1)	7726(1)	7630(1)	43(1)
Cl(1)	5059(1)	6679(1)	6687(1)	64(1)
Cl(2)	6916(1)	8812(1)	8444(1)	55(1)
Cl(3)	6814(1)	8506(1)	5861(1)	77(1)
P	2597(1)	7071(1)	4543(1)	45(1)
O(1)	3373(2)	5587(2)	5146(2)	53(1)
O(2)	1699(2)	7410(2)	3543(2)	63(1)
O(3)	1627(3)	8022(3)	5256(2)	77(1)
N	4907(2)	7079(3)	3496(2)	40(1)
C(1)	3628(3)	7915(3)	3983(3)	44(1)
C(2)	5829(4)	7721(4)	3324(3)	51(1)
C(3)	7136(4)	6910(4)	2813(4)	65(1)
C(4)	6920(5)	6771(6)	1709(4)	75(1)
C(5)	5990(5)	6139(5)	1890(4)	71(1)
C(6)	4690(4)	6943(4)	2404(3)	53(1)
C(7)	1653(5)	6349(5)	3207(4)	72(1)
C(8)	710(7)	5886(8)	3866(7)	98(2)
C(9)	418(7)	7920(9)	5800(7)	102(3)
C(10)	68(10)	8335(17)	6748(8)	128(5)
C(91)	1216(24)	7630(21)	6415(19)	87(8)
C(101)	510(27)	7294(36)	6851(21)	76(10)
C(11)	7205(3)	5704(3)	8724(2)	43(1)
C(12)	8548(4)	5261(4)	8942(3)	58(1)
C(13)	9330(4)	3941(4)	9657(4)	69(1)
C(14)	8803(4)	3061(4)	10194(3)	67(1)
C(15)	7483(5)	3480(4)	10007(3)	67(1)
C(16)	6683(4)	4797(3)	9265(3)	54(1)
C(21)	3941(3)	9036(3)	8041(3)	44(1)
C(22)	3695(4)	9372(4)	9049(3)	54(1)
C(23)	2408(4)	10081(4)	9388(4)	65(1)
C(24)	1331(4)	10492(4)	8728(4)	68(1)
C(25)	1553(4)	10204(4)	7719(4)	68(1)
C(26)	2847(4)	9471(3)	7379(3)	56(1)

TABLE II

Principal bond lengths / Å and angles / ° in structure **II**

Bond lengths / Å			
Sn–C(11)	2.129(3)	P–C(1)	1.797(3)
Sn-C(21)	2.133(3)	O(2)–C(7)	1.454(5)
Sn–Cl(3)	2.353(1)	O(3)–C(91)	1.44(2)
Sn–Cl(1)	2.528(1)	O(3)–C(9)	1.483(6)
Sn–Cl(2)	2.545(1)	N–C(1)	1.481(4)
P–O(1)	1.459(2)	N–C(6)	1.495(4)
P–O(3)	1.554(2)	N–C(2)	1.514(4)
P–O(2)	1.556(2)	N–H(1)	0.82(3)
Bond angles / °			
C(11)–Sn–C(21)	123.9(1)	O(1)–P–C(1)	112.9(1)
C(11)–Sn–Cl(3)	116.79(9)	O(3)–P–C(1)	98.9(2)
C(21)–Sn–Cl(3)	119.33(9)	O(2)–P–C(1)	107.6(2)
C(11)–Sn–Cl(1)	90.23(9)	C(7)–O(2)–P	123.5(2)
C(21)–Sn–Cl(1)	90.66(9)	C(91)–O(3)–P	128.9(8)
Cl(3)–Sn–Cl(1)	88.25(4)	C(9)–O(3)–P	122.6(3)
C(11)–Sn–Cl(2)	91.00(9)	C(1)–N–C(6)	112.1(3)
C(21)–Sn–Cl(2)	92.10(9)	C(1)–N–C(2)	109.6(2)
Cl(3)–Sn–Cl(2)	87.49(4)	C(6)–N–C(2)	110.8(3)
Cl(1)–Sn–Cl(2)	175.66(3)	C(1)–N–H(1)	112(2)
O(1)–P–O(3)	117.4(1)	C(6)–N–H(1)	106(2)
O(1)-P-O(2)	114.4(1)	C(2)-N-H(1)	106(2)
O(3)-P-O(2)	104.2(2)		

atom can be classified here as the distorted octahedron. The last four items correspond to the essentially isolated trigonal bipyramid, and the remaining six – to the distorted trigonal bipyramid with an additional Sn···Cl contact near the equatorial plane of the bipyramid. An example of such dimer composing structure **I** is presented in Figure 3. In full accordance with the theory of hypervalent bonds,[17] the angle C–Sn–C constricts and the lengths of equatorial and terminal axial bonds Sn–Cl diverge with the reduction of secondary interaction Sn···Cl. An interesting feature of structures **I**, FIPGEQ, and QUCMSN (here and further on see footnote to Table III) is that the axial Sn–Cl bond not involved in the secondary Sn···Cl interaction is longer than the other axial bond. This occurs owing to specific interactions

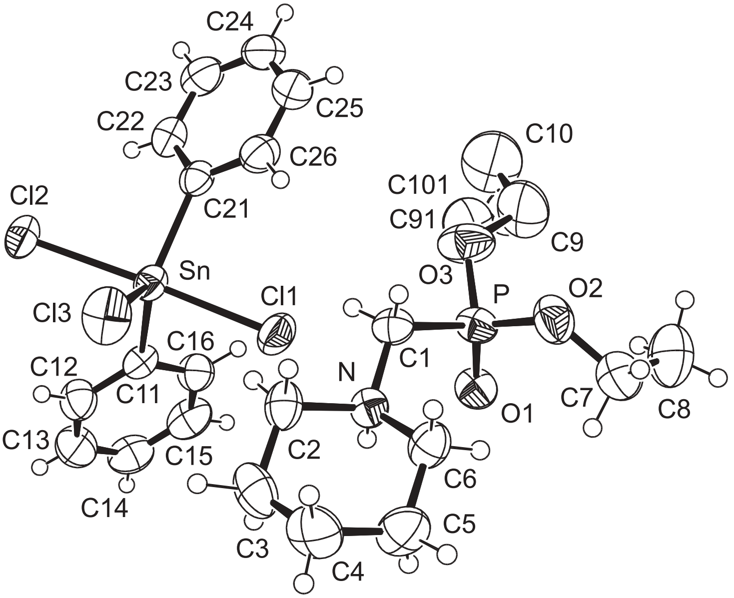

Figure 1. ORTEP drawing (ellipsoids of 50% probability) and atom labelling scheme of **II**.

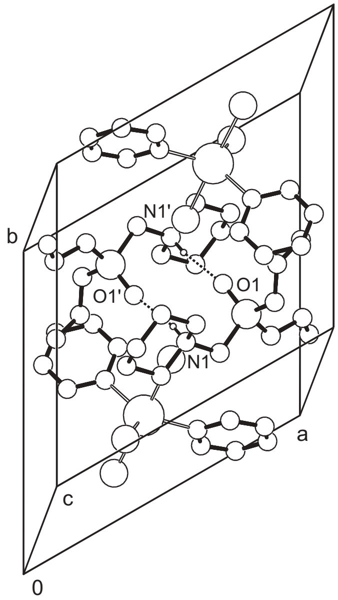

Figure 2. Content of the unit cell of **II**.

TABLE III

Principal geometric parameters of dimerized and isolated anions $[R_2SnCl_3]^-$; the length of secondary contact Sn···Cl, equatorial and axial bond lengths Sn–Cl$_{eq}$ and Sn–Cl$_{ax}$ [a] and the angle C–Sn–C

Structure [b]	Sn···Cl	Sn–Cl$_{eq}$	Sn–Cl$_{ax}$	C–Sn–C	Ref.
	Å	Å	Å	deg	
KUVGOX	2.899	2.472	2.836, 2.523	167	7
FUPTEP	2.944	2.440	2.759, 2.488	165	8
FEHNEL	3.205	2.405	2.773, 2.491	160	9
FUPTIT	3.259	2.406	2.623, 2.575	156	8
DAHYIU	3.370	2.432	2.687, 2.564	154	10
QUCMSN	3.486	2.407	2.560, 2.585	152	11
FIPGEQ	3.585	2.381	2.589, 2.649	142	12
I	3.824	2.361	2.494, 2.766	138	2
SNTPYR10	> 4.75	2.323	2.526, 2.565	141	13
HAWHOC	> 5.0	2.343	2 × 2.622	141	14
II	> 5.0	2.353	2.528, 2.545	124	this work
LEPFAN	> 6.0	2.378	2.517, 2.531	127	15

[a] For dimerized anions, the first value corresponds to the bond involved in the secondary interaction, and the second to the terminal axial bond.

[b] Refcodes from the Cambridge Crystallographic Data Base:[16]

KUVGOX – $[Me_2SnCl_3]^-$, $[C_{19}H_{18}NO_2]^+$, H_2O;

FUPTEP – $Me_2SnCl_3^-$, $\{Rh[C_5H_3N(C_3H_5)_2](C_8H_{12})\}^+$, CH_2Cl_2;

FEHNEL – $[M\varepsilon_2SnCl_3]^-$, $[Pt(PEt_3)_2(N_2S_2H)]^+$;

FUPTIT – $[Me_2SnCl_3]^-$, $\{Rh[C_5H_3N(C_3H_5)_2]\,(C_8H_{12})\}^+$;

DAHYIU – $[Me_2SnCl_3]^-$, $[C_6H_4S_4]^+$;

QUCMSN – $[Me_2SnCl_3]^-$, $[C_9H_8N]^+$;

FIPGEQ – $[Me_2SnCl_3]^-$, $[C_{14}H_8S_4]^+$;

SNTPYR10 – $[Me_2SnCl_3]^-$, $\{SnMe_2Cl[C_5H_3N(C_5H_4N)_2]\}^+$;

HAWHOC – $[Et_2SnCl_3]^-$, $2\{SnEt_2[C_5H_3N(C_8H_8N_3O)_2]\}^{2+}$, $3Cl^-$, $2H_2O$;

LEPFAN – $[Ph_2SnCl_3]^-$, NEt_4.

between the terminal chlorine atom and cation: hydrogen bonds in **I** and QUCMSN and Cl···S contacts in FIPGEQ.

Comparison of the structures from Table III gives no easy explanation why some of these structures exhibit dimerization of anions whereas others do not. However, two details should be mentioned, *viz*: *i*) there are no examples of hydrogen-bonded pairs anion–cation among the structures contain-

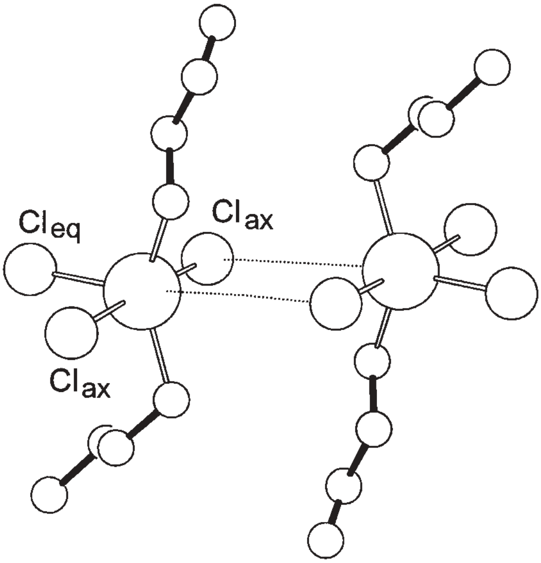

Figure 3. Anionic dimer composing structure **I**. Dotted lines represent secondary Sn···Cl interactions.

ing isolated anions; *ii*) both phenyltin derivatives (**II** and LEPFAN) form isolated anions. The capacity of pure diphenyltin halides to form secondary contacts Sn···Cl is also reduced, as compared to alkyltin halides. As for alkyl derivatives, the diversity of tin coordination polyhedra suggests that both edge-sharing octahedron and isolated trigonal bipyramid possess similar energies, so the choice between these forms is controlled by relatively weak crystal packing forces.

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SAŽETAK

Trigonsko-bipiramidni anion [Ph_2Cl_3Sn]$^-$ u strukturi *N*-[(dietilfosforil)metil]-piperidinijeva difeniltriklorstanata(IV)

Alexander V. Yatsenko, Ksenia A. Paseshnichenko, Valery S. Petrosyan, Natalia S. Yashina, Evgeny V. Grigoriev i Leonid A. Aslanov

U radu se opisuje priprava i određivanje kristalne i molekulske strukture kompleksnog ionskog spoja *N*-[(dietilfosforil)metil]-piperidinijeva difeniltriklorstanata(IV), $[C_{10}H_{23}NO_3P]^+$ $[C_{12}H_{10}Cl_3Sn]^-$. Difrakcijom rentgenskih zraka na jediničnom kristalu ustanovljeno je da spoj kristalizira u triklinskom sustavu s prostornom skupinom $P\bar{1}$ i parametrima jedinične ćelije: a = 11,416(2), b = 11,582(2), c = 12,491(2) Å, α = 69,82(2), β = 81,22(2), γ = 60,73(2)°, V = 1352,0(8) Å^3, Z = 2. Struktura je određena na temelju 4493 prikupljena difrakcijska maksimuma i utočnjena do faktora nepouzdanosti R = 0,027. Kristali su izgrađeni od izdvojenih trigonsko-bipiramidnih aniona i kationa dimeriziranih vodikovim vezama. U opisu strukture poseban je naglasak stavljen na geometriju kompleksnih aniona zbog nazočne međukationske interakcije Sn$\cdots$Cl.