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Preliminary Communication

The crystal structure of dichlorobis(2-imidazolidone)dimethyltin

P. Tavridou and U. Russo

Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Via Loredan 4, I-35131 Padova (Italy)

G. Valle

Centro di Ricerche sui Biopolimeri del CNR, Via Marzolo 1, I-35131 Padova (Italy)

D. Kovala-Demertzi

Department of Inorganic Chemistry, University of Ioannina, 451 10 Ioannina (Greece)

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Abstract

The results of a single-crystal X-ray diffraction study of the 1:2 adduct between dichlorodimethyltin(IV) and 2-imidazolidone are reported, together with some preliminary IR data. The complex is hexacoordinate and with a distorted *cis*-octahedral geometry.

The imidazoline system, part of the histidine molecule, contains a ring which is the parent of several compounds with a great pharmaceutical importance [1–5]. 2-Imidazolidone, Himio, is a closely related compound that contains a ketonic oxygen moiety in addition to the nitrogen. As a consequence, it can coordinate in various ways, depending on pH and reaction conditions. In previous studies [6–8] we reported several complexes of tin(II) and tin(IV) with derivatives of urea and thiourea, which possess the same coordination possibilities as 2-imidazolidone. Coordination numbers 5 and 6, and *cis* and *trans* arrangements, proposed for these complexes on the basis of IR and Mössbauer spectra and of X-ray crystal data, were attributed to the steric hindrance of the various ligands. As an extension of our research on tin compounds with pharmacological properties [9], we now describe preliminary spectroscopic data and the X-ray crystal structure of $[SnMe_2Cl_2(Himio)_2]$ (Himio = 2-imidazolidone). We wish to check the possibility that compounds with two Sn–O bonds, like those with two Sn–N bonds, have some biological activity. Such activity might be related to the O–Sn–O bond angle, as the N–Sn–N angle appears to be [10].

The compound was obtained by heating a dichloromethane solution of Himio and of $SnMe_2Cl_2$ in 1:1 molar ratio under reflux. A white solid was slowly formed on cooling. This was filtered, washed with solvent, and dried under vacuum. (Found: C, 24.43; H, 4.67; N, 14.20. $C_8H_{18}Cl_2O_2N_4Sn$ calcd.: C, 24.52; H, 4.63; N, 14.30%). Crystals suitable for X-ray study were obtained by slow solvent evaporation.

The crystals are monoclinic with $a = 10.675(2)$, $b = 8.545(1)$, $c = 16.288(2)$ Å, $\beta = 98.3(1)°$, $V = 1470.2(5)$ Å^3, D_o and $D_c = 1.75$ and 1.77 g/cm^3, $F(000) = 776$, space group $P2_1/a$, $Z = 4$. Intensity data were collected on a Philips PW 1100 four-circle diffractometer in the range $5 < 2\theta < 56°$ with Mo-Kα radiation. By using the criterion $F \geq 3\sigma(F)$, 2161 of the 2387 recorded intensities were independent and observable. Lorenz and polarisation corrections were applied, but not absorption corrections. The structure was solved using a three-dimensional Patterson-Fourier synthesis. A full-matrix least-squares refinement on F was computed and the function $\Sigma w[|F_o| - |F_c|]^2$ in which $w = 1.0/[\sigma^2(F) + 0.00166F^2]$ was minimized. The SHELX76 program [11] and the usual scattering factors therein enclosed were used. The non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were located from a difference Fourier map, but not refined. The final R value is 0.025. Fractional atomic coordinates for non-hydrogen atoms are reported in Table 1, while the Tables of observed and calculated structure factors can be obtained from the authors. Other data can be obtained from the Cambridge Crystallographic Dato Centre.

Bond distances and angles are reported in Tables 2 and 3 and the crystal structure is shown in Fig. 1. The tin atom has octahedral coordination with *trans* methyl groups and *cis* chlorine atoms. This arrangement is consistent with the IR spectra that show only ν_s(Sn–C) absorption at 580 cm^{-1} and two bands at 249 and 253 cm^{-1} attributable to ν_s(Sn–Cl) and ν_{as}(Sn–Cl). The Himio is coordinated by the oxygen atom, as inferred from the shift (from 1660 to 1650 cm^{-1}) of ν(C=O) due to the weakening of the double bond character as a consequence of the formation of the Sn–O bond.

Correspondence to: Professor U. Russo.

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TABLE 1. Fractional atomic coordinates for non-hydrogen atoms with standard deviations in parenthesis

Atom	*x*	*y*	*z*
Sn	0.50002(2)	0.00996(2)	0.75186(1)
Cl(1)	0.48432(9)	0.28174(10)	0.69513(5)
Cl(2)	0.48997(9)	0.09291(10)	0.89699(5)
O(1)	0.50179(23)	−0.26021(26)	0.79256(15)
O(2)	0.51848(24)	−0.07825(28)	0.61200(14)
N(1)	0.56209(33)	−0.48524(31)	0.86337(20)
N(2)	0.62429(37)	−0.26498(37)	0.92153(21)
N(3)	0.42846(37)	−0.32412(37)	0.61048(21)
N(4)	0.40288(34)	−0.18848(36)	0.49745(18)
C(1)	0.55751(31)	−0.33108(35)	0.85421(20)
C(2)	0.64723(45)	−0.53275(46)	0.93622(28)
C(3)	0.66888(48)	−0.37939(46)	0.98440(26)
C(4)	0.45572(33)	−0.18867(37)	0.57631(20)
C(5)	0.34224(45)	−0.33648(46)	0.47267(24)
C(6)	0.33900(46)	−0.41522(49)	0.55624(24)
C(7)	0.30473(44)	−0.03254(66)	0.72362(33)
C(8)	0.69886(48)	0.00208(65)	0.76625(38)

TABLE 2. Bond distances (Å) with estimated standard deviations in parentheses

Sn–Cl(1)	2.4961(9)	Sn–Cl(2)	2.485(1)
Sn–O(1)	2.401(2)	Sn–O(2)	2.434(2)
Sn–C(7)	2.101(5)	Sn–C(8)	2.103(5)
O(1)–C(1)	1.248(4)	O(2)–C(4)	1.251(4)
N(1)–C(1)	1.326(4)	N(1)–C(2)	1.445(5)
N(2)–C(1)	1.343(5)	N(2)–C(3)	1.446(5)
N(3)–C(4)	1.334(5)	N(3)–C(6)	1.433(6)
N(4)–C(4)	1.326(4)	N(4)–C(5)	1.451(5)
C(2)–C(3)	1.528(6)	C(5)–C(6)	1.523(6)

TABLE 3. Bond angles (°) with estimated standard deviations in parentheses

C(7)–Sn–C(8)	166.6(2)	O(2)–Sn–C(8)	83.0(2)
O(2)–Sn–C(7)	87.3(2)	O(1)–Sn–C(8)	88.3(2)
Cl(2)–Sn–C(8)	94.9(2)	O(1)–Sn–O(2)	87.83(8)
O(1)–Sn–C(7)	82.1(2)	Cl(2)–Sn–C(7)	94.6(2)
Cl(2)–Sn–O(2)	177.38(9)	Cl(2)–Sn–O(1)	90.65(6)
Cl(1)–Sn–C(8)	94.8(2)	Cl(1)–Sn–C(7)	93.9(2)
Cl(1)–Sn–O(2)	87.24(6)	Cl(1)–Sn–O(1)	173.79(7)
Cl(1)–Sn–Cl(2)	94.41(3)	Sn–O(1)–C(1)	132.3(2)
Sn–O(2)–C(4)	123.9(2)	C(1)–N(1)–C(2)	112.3(3)
C(1)–N(2)–C(3)	112.1(3)	C(4)–N(3)–C(6)	112.3(3)
C(4)–N(4)–C(5)	112.2(3)	N(1)–C(1)–N(2)	108.6(3)
O(1)–C(1)–N(2)	126.0(3)	O(1)–C(1)–N(1)	125.3(3)
N(1)–C(2)–C(3)	102.2(3)	N(2)–C(3)–C(2)	101.9(3)
N(3)–C(4)–N(4)	108.5(3)	O(2)–C(4)–N(4)	125.0(3)
O(2)–C(4)–N(3)	126.5(3)	N(4)–C(5)–C(6)	101.7(3)
N(3)–C(6)–C(5)	102.2(4)		

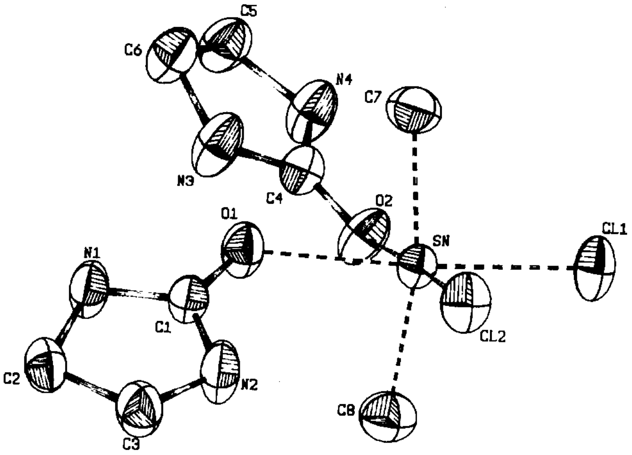

Fig. 1. Perspective view of the title compound with the atom numbering scheme.

The coordination polyhedron is slightly distorted as the C–Sn–C angle is 166.6(2)° and the two Cl–Sn–O angles are 177.38(9) and 173.79(7)°, respectively. The Sn–C bond distances (2.101(5) and 2.103(5) Å) compare very well with those reported for [$SnMe_2Cl_2TMU$] [7] (TMU = tetramethylurea) (2.100(7) and 2.107(7) Å), while the Sn–O distances (2.401(2) and 2.434(2) Å) are slightly longer (2.357(4) Å) and the Sn–Cl (2.4961(9) and 2.485(1) Å) virtually identical with the longest bond in the [$SnMe_2Cl_2TMU$] (2.497(2) Å), but much shorter than in [$SnMe_2Cl_2$2DMTU] (DMTU = dimethylthiourea) (2.589(2) Å) [8]. The four equatorial donor atoms form a slightly distorted plane in which the tin atom is also found. The C–O bond distance in the Himio (1.248(4) and 1.251(4) Å) is slightly shorter than in [$SnMe_2Cl_2TMU$] (1.269(7) Å) and in [$SnPh_3Cl$-TMU] (1.26(2) Å), suggesting a weaker interaction with tin.

A very simple net of hydrogen bonds contributes to the cohesion of the structure. The crystal packing is mainly determined by the Himio nitrogen atoms in N(1)–H ⋯ Cl(1) (x, $y-1$, z) (3.392(3) Å) and in N(4)–H ⋯ O(2) ($1-x$, $-y$, $1-z$) (3.084(4) Å). Two more intramolecular hydrogen bonds (N(2)–H ⋯ Cl (2), 3.377(3) Å, and N(3)–H ⋯ O(1), 3.006(4) Å, contribute to the rigidity of the molecule.

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