Inorganic Chemistry Communications 14 (2011) 133–136

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Synthesis, characterization and behaviour in solution of organotin complexes based on azole ligands. Single crystal X-ray study of dichlorodimethylbis(1,2,3-benzotriazole)tin(IV)

Corrado Di Nicola [a], Fabio Marchetti [b], Claudio Pettinari [a,*], Brian W. Skelton [c], Allan H. White [c]

[a] School of Pharmacy, Università degli Studi di Camerino, via S Agostino 1, 62032 Camerino MC, Italy
[b] School of Science and Technology, Università degli Studi di Camerino, via S Agostino 1, 62032 Camerino MC, Italy
[c] Chemistry M313, School of Biomedical, Biomolecular and Chemical Sciences, The University of Western Australia, Crawley, WA 6009, Australia

ARTICLE INFO

Article history:
Received 21 July 2010
Accepted 7 October 2010
Available online 15 October 2010

Keywords:
Benzotriazole
Indazole
Organotin(IV)
Crystal structure
ESI MS

ABSTRACT

Nine new organotin complexes, namely $[SnR_2XY(BtzH)_2]$ (**1**: R = Me, X = Y = Cl, **2**: R = Me, X = Y = Br, **3**: R = ^{n}Bu, X = Cl, Y = OH; **4**: R = Ph, X = Y = Cl; **5a**: R = Me, X = Y = NO_3; **5b**: R = Me, X = Y = ClO_4) and $[SnR_2X_2(5\text{-}NO_2indH)_2]$ (**6**: R = Me, X = Cl; **7**: R = ^{n}Bu, X = Cl; **8**: R = Me, X = 5-NO_2ind) were obtained by reaction of SnR_2X_2 with BtzH (1,2,3-benzotriazole) and 5-NO_2indH (5-nitroindazole). These compounds were characterized by IR, NMR and ESI MS, and **1** is shown by a single crystal X-ray study to comprise mononuclear centrosymmetric molecules, all pairs of ligands being mutually opposed in a quasi-octahedral coordination sphere. Sn–Cl, C, N are 2.5700(5), 2.108(2), 2.357(2)Å. A new triclinic ($P\bar{1}$) polymorph of the binuclear $[\{^tBu_2ClSn(\mu\text{-}OH)\}_2]$, **9** is also described (cf. the earlier monoclinic ($P2_1/c$)). The unit cell contents comprise a pair of centrosymmetric dimers: Sn–O are 2.042(4)–2.215(4), Sn–Cl 2.489(2), 2.491(2), Sn–C 2.166(6)–2.203(7) Å, O–Sn–O 68.4(2) (x2), and Sn–O–Sn 111.6(2)° (x2).

The chemistry of SnR_nX_{4-n} derivatives of azoles is well known [1], but to date there has been no structural report concerning tin and organotin(IV) complexes of benzotriazoles and, also, 5-nitroindazole, both of which occupy important positions amongst heterocyclic rings for their relevance to the chemistry, for example, of natural products [2]. Here we report the syntheses, structural and spectroscopic characterization for several new complexes obtained from the reaction of SnR_2X_2 (R = Me, ^{n}Bu; Ph, X = Cl, or Br) acceptors and 1,2,3-benzotriazole or 5-nitroindazole.

Preparation of the organotin complexes is usually attempted by using a variety of azole ligand to organotin(IV) ratios [3,4], in order to determine if more than one kind of derivative is afforded between L (L = BtzH or 5-NO_2IndH) and a specific organotin(IV) acceptor. Interaction between excess azole ligand L and SnR_2X_2in organic solvent (diethyl ether, dichloromethane, acetonitrile, ethanol) gave the 2:1 adducts **1–4, 6** and **7** [3,4] according to Eq. (1):

$$2L + SnR_2X_2 \rightarrow [SnR_2X_2(L_2)] \qquad (1)$$

No adduct has been isolated from the reaction of L with R_3SnX. The reaction between $Sn^nBu_2Cl_2$ and BtzH seemed not to produce any identifiable product. However when a solution containing both reactants was exposed to moisture for a long time, the adduct $[Sn^nBu_2Cl(OH)(BtzH)_2]$ (**3**) formed, where one chloride had been replaced by a hydroxide group. Reaction of **1** with $AgNO_3$ in acetone gave immediately the derivative $[SnMe_2(NO_3)_2(BtzH)_2]$ **5a**, upon substitution of both Cl groups from the tin coordination sphere [5]. An analogous species $[SnMe_2(ClO_4)_2(BtzH)_2]$, **5b**, was obtained when **1** was reacted with $AgClO_4$. The complexes **1–7** are poorly soluble in chlorinated solvents and acetone and moderately soluble in DMSO. Several attempts to obtain crystals of adducts **1–7** in suitable form for X-ray studies failed with the exception of **1**, amorphous powders or well-known hydrolysis products being isolated. It is noteworthy that the reaction of 5-NO_2IndH with $SnMe_2Br_2$ gives compound **8**, where both Br^- ions have been replaced by a deprotonated 5-NO_2Ind [4]. The occurrence of a hydrolysis reaction yielding the hydroxo species **3** is confirmed by the acquisition of compound **9**, $[\{^tBu_2ClSn(\mu\text{-}OH)\}_2]$ [6], formed when the reaction between BtzH and $Sn(^tBu)_2Cl_2$ was carried out in ethanol for 12 h. The IR spectra of the ligands and their complexes have also been recorded. In the 3100–2800 cm^{-1} region the ligands exhibit broad bands typical of N–H stretching, but always shifted, suggesting an important consequence of coordination to tin. The positions and the broadening of the N–H stretching bands are also consistent with the presence of hydrogen bonds between the N–H moieties and the halide groups [7]. The appearance of only a single Sn–C stretching vibration in the spectra of the dimethyltin(IV) complexes **1**, **2**, and **6**, is in accordance with a *trans*-octahedral disposition of the two alkyl groups [8]. The ^{1}H NMR spectra of the

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[*] Corresponding author. Tel.: +39 0737 402234; fax: +39 0737 637345.
E-mail address: claudio.pettinari@unicam.it (C. Pettinari).

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doi:10.1016/j.inoche.2010.10.004

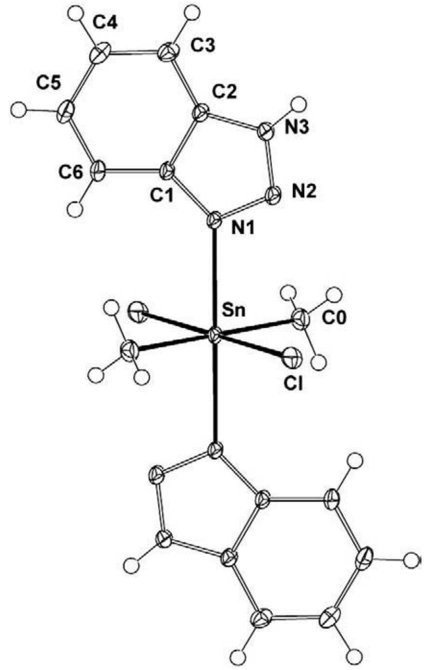

Fig. 1. Projection of a single centrosymmetric molecule of *trans*-[$Me_2Cl_2Sn(C_6H_5N_3)_2$] (**1**). Sn–C(0), N(1), and Cl are 2.108(2), 2.357(2), and 2.5700(5) Å; C(0)-Sn-N(1), Cl, and N(1)–Sn–Cl are 88.80(7), 88.84(7), and 90.42(4)°. H(6)…Cl′ is 3.2 Å (est.). With Sn at (0.5, 0.5, 0.5), the aromatic ligand stack interleaves up crystallographic *a* (7.0156(6) Å). Non-hydrogen atoms are shown with 50% probability amplitude displacement envelopes, hydrogen atoms having arbitrary 0.1 Å radii.

complexes, recorded in MeOD or DMSO, due to the poor solubility of **1**–**8** in $CDCl_3$, suggest almost complete dissociation into the starting reagents, the Δ values (difference in chemical shift for the same type of proton in the free base and its organotin complex) being in the range 0.1–0.15 ppm. The spectrum of **1** in acetone is also unusual, two different sets of signals due to the benzotriazole protons being detected. We hypothesize, also on the basis of the conductivity data which suggest partial ionic dissociation, that acetone could be able to displace one chloride from the tin coordination sphere, yielding a species such as [$SnMe_2Cl(acetone)(BtzH)_2$]$^+$ where the two BtzH groups experience two different environments, although we cannot exclude that this could be due to differing coordination modes of the two BtzH in solution. In the case of the nitrate and perchlorate species **5a,b** the Δ is greater suggesting greater stability of these species in solution. The measured δ(^{119}Sn) and tin-proton coupling constant values for selected compounds do not fit clearly into the reported ranges of values of six-coordinate organotin(IV) compounds, but are in accordance with the dissociation proposed on the basis of ^{1}H NMR data [9,10].

Table 1
Benzotriazole ligand non-hydrogen atom geometries; the two values in each entry are for the present tin(IV) complex, (**1**), and the means of those for the free ligand, reported in Ref. [15].

Atoms	Parameter	Atoms	Parameter
Distances (Å)			
C(1)–N(1)	1.376(3), 1.369(3)	C(2)–C(3)	1.392(3), 1.386(4)
N(1)–N(2)	1.308(2), 1.308(3)	C(3)–C(4)	1.378(3), 1.352(7)
N(2)–N(3)	1.322(2), 1.343(5)	C(4)–C5))	1.412(4), 1.391(4)
C(2)–N(3)	1.358(2), 1.352(5)	C(5)–C(6)	1.378(3), 1.358(4)
C(1)–C(2)	1.397(3), 1.382(3)	C(1)–C(6)	1.396(3), 1.398(4)
Angles (°)			
C(1)–N(1)–N(2)	109.1(2), 108.1(6)	C(2)–C(1)–C(6)	121.0(2), 120.4(2)
N(1)–N(2)–N(3)	108.4(2), 108.5(7)	C(1)–C(2)–C(3)	122.9(2), 122.3(5)
N(2)–N(3)–C(2)	111.3(2), 110.6(5)	C(2)–C(3)–C(4)	115.7(2), 116.4(2)
N(3)–C(2)–C(1)	104.3(2), 104.3(2)	C(3)–C(4)–C(5)	121.9(2), 122.2(3)
C(2)–C(1)–N(1)	106.9(2), 108.5(4)	C(4)–C(5)–C(6)	122.2(2), 121.9(5)
N(1)–C(1)–C(6)	132.1(2), 130.9(7)	C(1)–C(6)–C(5)	116.3(2), 116.8(5)
N(3)–C(2)–C(3)	132.8(2), 133.4(6)		
Sn–N(1)–N(2)	114.5(1)	Sn–N(1)–C(1)	136.4(1)

The tin atom lies out of the C_6N_3 plane (χ^2 103) by 0.057(3) Å.

ESI MS spectra carried out in MeCN for complexes **1**, **2** and **4** exhibit some weak intensity signals due to the formation of species such as [$SnR_2Cl(BtzH)_2$]$^+$ upon chloride abstraction. The ESI MS spectra of **5a** shows a different pattern likely due to the presence of readily ionizable NO_3 groups. In fact in the positive spectrum we have found signals due not only to mononuclear species [$SnMe_2(NO_3)(BtzH)^+$] derived from NO_3 dissociation, but also signals due to

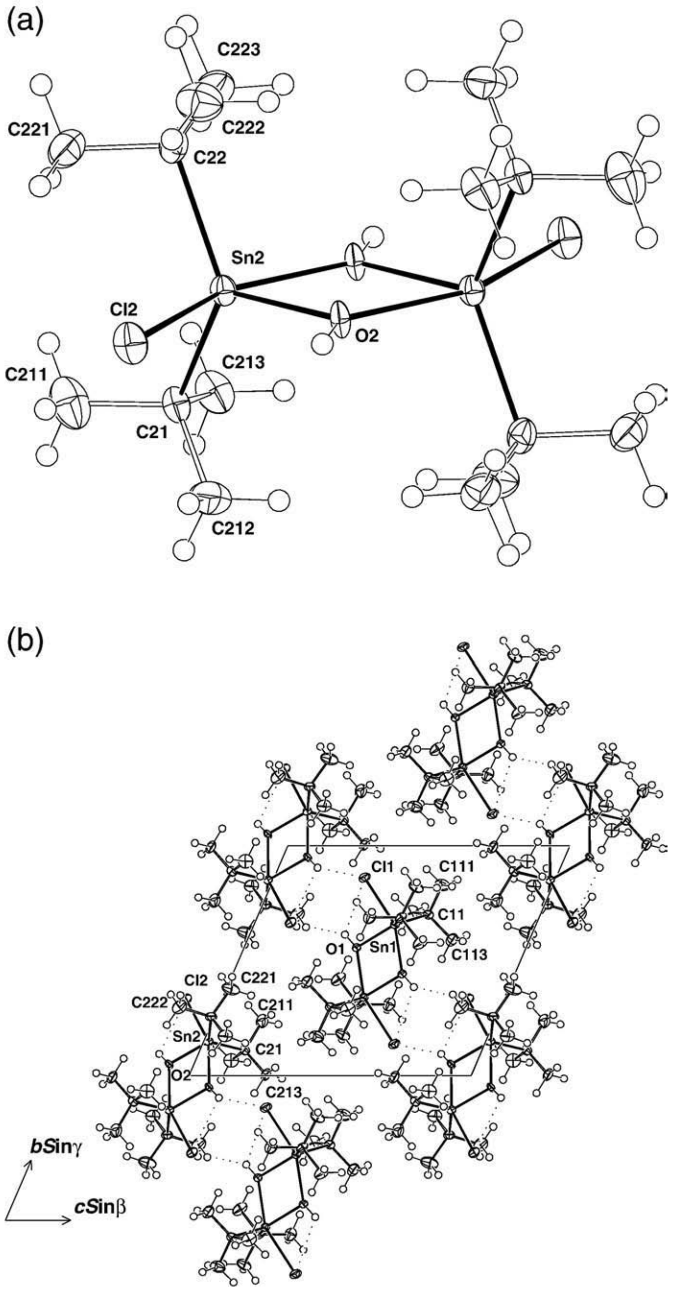

Fig. 2. (a) A projection of binuclear, centrosymmetric molecule 1 of [{^{t}Bu$_2$ClSn(μ-OH)}$_2$] (**9**) (molecule 2 is similar); non-hydrogen atoms are shown with 50% probability amplitude displacement envelopes, hydrogen atoms having arbitrary radii of 0.1 Å. (b) Unit cell contents, projected down *a*, showing the H…Cl interactions. The molecules are linked into two separate columns along *a*, each one associated with one of the independent components of the asymmetric unit.