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Synthesis and characterisation of organotin(IV) derivatives of ambidentate ligands containing nitrogen and sulphur donor atoms

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Abstract

A series of organotin(IV) derivatives of bis(pyrimidin-2-ylthio)methane (*ptm*), 1,2-bis(pyrimidin-2-ylthio)ethane (*pte*) and 1,6-bis(pyrimidin-2-ylthio)hexane (*pth*) have been prepared in dichloromethane at room temperature. The 2:1 (M/L) molar ratio compounds have a general formula of [$Sn_2Cl_x Ph_{8-x}L$] (x=2, 4, 6, 8; L=*ptm*, *pte* and *pth*). A 1:1 complex was also obtained by reacting $SnClPh_3$ with *pth*. The organotin derivatives were characterised by multinuclear NMR (^{1}H, ^{13}C and ^{119}Sn) and infrared spectroscopy, gel permeation chromatography (GPC), microanalysis and melting point. In the triphenyltin derivatives, **1**, **5**, **9** and **10** the tin atoms show a distorted trigonal-bipyramidal configuration where the ligand is monodentate towards the metal atom. In the compounds **2–4**, **6–8** and **11–13**, the tin atoms each exhibit a distorted octahedral configuration. Chelation is formed between the tin nucleus and the coordinating sulphur and nitrogen atoms. The correlation between the $^1J(^{13}C-^{119}Sn)$ and C-Sn-C bond angle indicates formation of 5-coordinate compounds.

Keywords: bis(pyrimidin-2-ylthio)alkane; gel permeation chromatography (GPC); infrared; organotin; polyfunctional ligands; ^{119}Sn NMR.

Introduction

In the past decades, biological properties of organotin compounds have been the focus of attention of inorganic chemists. Concern about these chemicals is related to their biomedical (Gielen, 1996, 2003; Gielen et al., 1999, 2005). Our research is particularly concerned in developing new organotin compounds using ligands of ambidentate character. In this context, (S,N)-compounds are motivating because of being flexible ligands and presenting a contrasting hardness and softness property between sulphur and nitrogen atoms. Complexes of the first and second row of transition metals with tris- and bis(pyridin-2-ylthio)methane have been reported (Adhikary and Lucas, 1994; Barclay et al., 1998; Matthews et al., 1998; Chou et al., 1999). These ligands are capable of coordinating to metal centres, leading to stable chelating rings. For instance, the reaction between copper(II) chloride and tris(pyridin-2-ylthio)methane led to the first example of a stable compound containing a Cu-C(sp^3) bond (Kinoshita et al., 2003; Miyamoto et al., 2005). The metal is 5-coordinate, forming three chelating rings with three coordinating nitrogen atoms from the ligand. Recently, organotin(IV) adducts of bis(pyridin-2-ylthio)methane and tris(pyridin-2-ylthio)methane have also been reported (Pellei et al., 2006).

Following our interest in coordination chemistry, three bis(pyrimidin-2ylthio)alkanes of general formula $(pymS)_2(CH_2)_n$ (n=1, 2, 6) (Figure 1) have been prepared for further complexation reactions with organotin precursors ($SnCl_xPh_{4-x}$; x=1, 2, 3) and $SnCl_4$. These ligands designated as bis(pyrimidin-2-ylthio)methane (*ptm*), 1,2-bis(pyrimidin-2-ylthio)ethane (*pte*) and 1,6-bis(pyrimidin-2-ylthio)hexane (*pth*) were separated in moderate yields.

Results and discussion

The bis(pyrimidin-2-ylthio)alkanes are soluble in organic solvents such as methanol, acetonitrile, acetone, dichloromethane, dimethylformamide (DMF) and dimethylsulphoxide (DMSO), as are their organotin(IV) derivatives, except complex **7**. The latter was soluble in DMF and DMSO only. The solubility of these organotin compounds is reminiscent of bis(pyridin-2ylthio)alkanes analogues (Pellei et al., 2006). All bis(pyrimidin-2-ylthio)alkane-organotin derivatives were synthesised in a 2:1 molar ratio, except complex **9**. These compounds are air stable materials, except complex **7**. Good yield of complex **1** was also achieved by heating a solid mixture of triphenyltin(IV) chloride with bis(pyrimidin-2-ylthio) methane under inert atmosphere.

Infrared spectroscopy

The formation of bis(pyrimidin-2-ylthio)alkanes has been confirmed by the absence of the SH stretching frequency in the region of 2550 cm^{-1}. The infrared spectra of the three novel ligands exhibited strong absorptions in the region of 1570 cm^{-1}, owing to ν(C=N+C=C) ring deformation (Pellei et al., 2006). An infrared shift from 39 to 49 cm^{-1} towards high frequency has been observed for complexes **3**, **4**, **6**, **7**, **8**, **11**, **12** and **13** (group A). This remarkable shift is evidence of a strong interaction between the tin(IV) nucleus and the

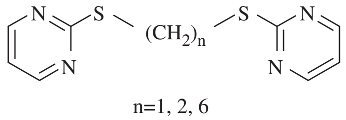

Figure 1 Molecular structure of bis(pyrimidin-2-ylthio)alkanes.

pyrimidyl moiety from the ligand. However, a negligible shift, within the equipment resolution (1–4 cm^{-1}), was observed for complexes **1**, **2**, **5**, **9** and **10** (group B). Similar remarks have been reported for monodentate diphenyltin(IV) derivative of salicylaldehyde-thiosemicarbazonato (Casas et al., 1994). Chelation and monodentate coordination modes are likely to occur, based on these infrared shifts. In this context, the compounds from group A and group B may have the ligand acting in a bidentate and monodentate coordination mode, respectively.

An absorption in the region of 456 cm^{-1} is associated with the stretching frequency of a Sn-N bond in all compounds synthesised. An infrared band in the region of 405 cm^{-1} was revealed in the spectra of group A, except **13**. This infrared frequency correlates with formation of a Sn-S bond as observed for thiolate- and 2-mercaptopyrimidine-organotin(IV) derivatives (Domazetis et al., 1981; Nakamoto, 1997; Ma et al., 2006; Tarassoli et al., 2006). The combination of these data reinforces the view that the pyrimidinthioalkanes are bidentate towards the metal centre in the compounds of group A.

The Sn-Cl stretching mode has been exhibited in the region of 335 cm^{-1} as a single band for the triphenyltin(IV) derivatives, complexes **1**, **5**, **9** and **10**. A sharp absorption has also been found in the spectrum of **6** and **11**, diphenyltin(IV) derivatives. This is indicative of *trans* isomerisation of chlorine atoms in the latter two compounds. Two Sn-Cl bands were also revealed in the spectrum of **2**, a diphenyltin(IV) derivative as well. In this case, the chlorine atoms are conceived as being in *cis* configuration. As the infrared spectrum of complex **2** did not exhibit a Sn-S band but a Sn-N one, the metal is presumably at the centre of a trigonal-bipyramidal arrangement. Owing to the presence of a Sn-S band in the spectrum of complexes **6** and **11**, the metal for these complexes is assumed to be at the centre of an octahedron. Two Sn-Cl bands were also exhibited in the spectra of phenyltin(IV) (**3**, **7**, **12**) and tetrachloridetin(IV) derivatives (**4**, **8**). These infrared bands are most likely related to formation of *fac/mer* isomers in the phenyltin(IV) derivatives (Von Poelhsitz et al., 2002). The phenyl group in these complexes (**3**, **7** and **12**) may occupy an axial or equatorial position of an octahedron. Based on these two Sn-Cl infrared bands, the tetrachloride derivatives (**4**, **8**) presumably have two chlorine atoms in *cis* and two in *trans* position of an octahedron. An exception, however, has occurred for complex **13**, a tetrachloride derivative. The infrared spectrum of this compound revealed one sharp Sn-Cl absorption instead of two. This is symptomatic of four chlorine atoms in *trans* position, most likely in the equatorial position of an octahedron. Proposed octahedral and trigonal-bypyramidal arrangements for the tin(IV) compounds are shown in Figure 2.

NMR spectroscopy

The ^{1}H NMR revealed resonance signals for pyrimidyl, phenyl and alkane moieties within the expected chemical shift range of aromatic and aliphatic fragments. A significant upfield chemical shift, related to the pyrimidyl moiety, was observed for compounds of group A, in comparison with free ligands. Similar chemical shifts did not occur for complexes of group B. This pattern is evidence of strong as well as weak interactions between the pyrimidyl fragment and the metal centre in groups A and B, respectively.

Significant chemical shifts have been revealed in the ^{13}C NMR spectra of group A in comparison with those of group B. Analogous NMR data are described in the literature for a Cd(II)-complex derivative of bis(pyridin-2-ylthio)methane (Amoedo-Portela et al., 2003). Complex **6** decomposes in solution. The ^{1}H chemical shift observed for this compound is reminiscent of *pte* ligand along with that of free triphenyltin(IV) precursor. In addition, the ^{13}C NMR showed poor NMR data even after long acquisition time.

The correlation between C-Sn-C angle and $^{1}J(^{13}C\text{-}^{119}Sn)$ is a useful method for determining the geometric pattern around the tin(IV) nucleus (Lockhart et al., 1985; Lockhart and Manders, 1986; Caruso et al., 1994). These parameters are linearly linked which allow an insight into the stereochemistry of organotin(IV) compounds. The $^{1}J(^{13}C\text{-}^{119}Sn)$ depends on the donor ability of the solvent and the electronegative effect of the substituent. This method has been successfully applied to organotin(IV) compounds characterisation in the presence of coordinating and non-coordinating solvents (Mathiasch, 1981; Alallaf, 1986; Handlir et al., 1988). Considering that compounds of group B did not reveal a considerable ^{13}C NMR chemical shift, the structural arrangement around the metal has been evaluated based on the correlation between $^{1}J(^{13}C\text{-}^{119}Sn)$ and C-Sn-C bond angle. DEPT 35 NMR was the technique to assign the carbon atom directly attached to the metal centre. A solvent effect has been disregarded taking into account the non-coordinating properties of $CDCl_3$.

The $^{1}J(^{13}C\text{-}^{119}Sn)$, the calculated C-Sn-C and C-Sn-C bond angles from crystallographic data of several compounds are displayed in Table 1 for comparison. The $^{1}J(^{13}C\text{-}^{119}Sn)$ for the triphenyltin derivatives **1**, **5**, **9** and **10** is between the experimental values of **16**, **15** and **14**, 4- and 5-coordinate compounds. The calculated C-Sn-C bond angles follow the same tendency. In this context, these triphenyltin(IV) compounds most likely have the metal at the centre of a trigonal-bipyramidal arrangement. The C-Sn-C bond angles, obtained by X-ray diffraction, have low values in comparison with that of corresponding calculated ones (Bordinhao et al., 2006). This is not surprising as distorted geometries may give odd calculated values, as observed for an oxinate derivative (Lockhart et al., 1985). Complex **2**, by contrast, has a $^{1}J(^{13}C\text{-}^{119}Sn)$ value above that of **13**, **2h** and **4h** but below **1c** and **2d**, all 5-coordinate compounds. Again, the calculated C-Sn-C bond angle follows the same tendency. The low C-Sn-C value of **2** in comparison with **1c** and **2d** could be due to the stereochemistry of phenyl groups, which may occupy an axial position of a distorted trigonal-bipyramidal arrangement.

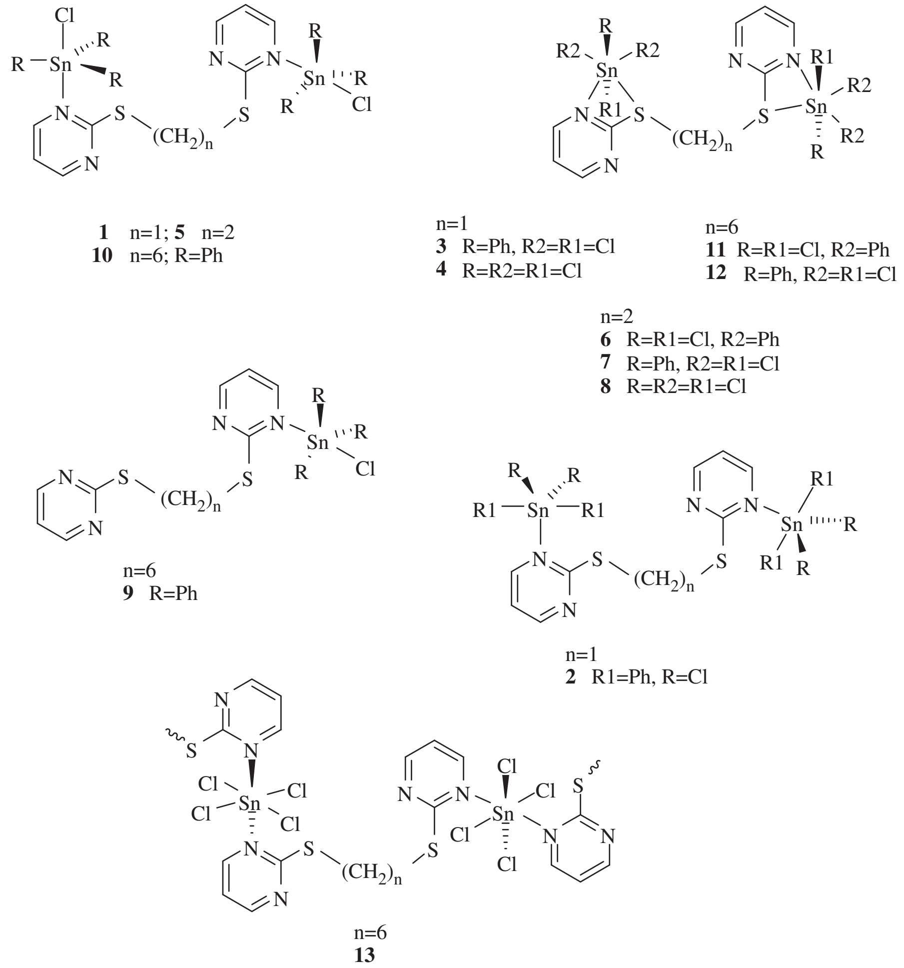

Figure 2 Possible structural arrangements of tin(IV)-bis(pyrimidin-2-ylthio)alkanes.

This is corroborated by the two Sn-Cl infrared bands of **2** at low frequency.

The $^1J(^{13}C\text{-}^{119}Sn)$ data described in the literature for 6-coordinate complexes are above 1005 Hz, as shown in Table 1. This excludes, therefore, compounds **1**, **2**, **5**, **9** and **10** from having a 6-fold coordination. By contrast, the $^1J(^{13}C\text{-}^{119}Sn)$ of 5-coordinate triphenyltin(IV) compounds ranges from 600 to 660 and 750 to 850 Hz, depending on the axial or equatorial position of phenyl groups (Holecek et al., 1983; Baul et al., 2001). In view of this, this range of $^1J(^{13}C\text{-}^{119}Sn)$ reinforces the view of the metal in **1**, **2**, **5**, **9** and **10** as 5-coordinate at the centre of a trigonal-bipyramidal arrangement (Gómez et al., 2003).

The ^{119}Sn NMR spectroscopy revealed peaks in the general range observed for 5-, 6- and 7-coordinated organotin compounds. The ^{119}Sn signals from **1**, **5**, **9** and **10** mismatches that of the metal precursor $SnClPh_3$ (δ=-44.7, CH_2Cl_2) as in **2**, a $SnCl_2Ph_2$ (δ=-32.0, CH_2Cl_2) derivative. The chemical shift of **1**, **2**, **5**, **9** and **10** is consistent with formation of 5-coordinate species in solution (Otera, 1981; Holecek et al., 1983; Singh et al., 1990). The chemical shift of **3** (in CH_3OH) is correlated to 6-coordinate organotin compounds but in **4**, **7**, **8** and **12** (in DMSO) the chemical shift can be related to both 6- and 7-coordinate compounds (Otera, 1981; Otera et al., 1982). The spectra of **4** and **8**, however, have exhibited an interesting spectral pattern. Signals at the same chemical shift appeared in the spectra of both complexes, in the range of -600 to -700. This suggests they have the tin(IV) core at the same magnetic environment, although they have been synthesised from *ptm* and *pte* ligands. In view of the fact that this range of chemical shift is generally linked to octahedral and pentagonal-bipyramidal arrangements, the molecular units have presumably 6- and 7-coordinate metal centres. In this case, a chemical equilibrium between 6- and 7-coordinate species is likely by an intramolecular metal-ligand bond (see Figure 3).

The spectra of **7** and **12** showed several resonance peaks of variable intensity in DMSO, a coordinating solvent. The chemical shift revealed by NMR is also consistent with 6- and 7-coordinate tin(IV) nuclei for these compounds. However, autoassociation due to solvent coordination is probably the reason for having several peaks in their spectra (Hani and Geanangel, 1982; de Mello et al., 2004). Every attempt to collect suitable crystals for X-ray diffraction of those organotin derivatives have failed. The crystals obtained and characterised by this technique have proved to be the starting metal precursors. This

Table 1 $^{1}J(^{13}C-^{119}Sn)$ (Hz) and C-Sn-C bond angles of organotin(IV) compounds.

Compound	$^{1}J(^{13}C-^{119}Sn)$	C-Sn-C[a]	C-Sn-C[b]	CN	References
1e (*trans*-dibutil)	1130	169.2(1)	175.8	hexacoord.	(a)
2h (*cis*-dibutil)	559.6	124.4(2)	125.8	pentacoord.	(a)
4h (*cis*-dibutil)$_{dist}$	566.4	116.9(2)	126.4	pentacoord.	(a)
2 [$Sn_2Cl_4Ph_4$(*ptm*)]	797.9	–	146.7	pentacoord.	This work
1c (*cis*-diphenyl)$_{dist}$	1005	125.8(3)	164.9	pentacoord.	(b)
2d (*cis*-diphenyl)$_{dist}$	984	128.8(2)	163.0	pentacoord.	(b)
13(1)[c] (*cis*-dimethyl)	624.5	121.2(2)	131.5	pentacoord.	(c)
1 [$Sn_2Cl_2Ph_6$(*ptm*)]	615.8	–	130.7	pentacoord.	This work
5 [$Sn_2Cl_2Ph_6$(*pte*)]	615.7	–	130.7	pentacoord.	This work
9 [$SnClPh_3$(*pth*)]	668.1	–	135.3	pentacoord.	This work
10 [$Sn_2Cl_2Ph_6$(*pth*)]	615.7	–	130.7	pentacoord.	This work
14(6)[c] (triphenyl)	786.4	118.5(1) 118.8(1) 121.1(1)	145.7	pentacoord.	(d)
15(2)[c] (triphenyl)$_{dist}$	564.6	113.18(8) 107.50(8) 106.17(5)	126.3	tetracoord.	(e)
16(1)[c] (triphenyl)$_{dist}$	562.9	113.2(2) 116.6(2) 113.5(2)	126.0	tetracoord.	(e)

[a]X-ray bond angles data; *dist*: distorted structure; NC: coordination number.

[b]Estimated C-Sn-C angle (deg) according to the Lockhart equation (Lockhart et al., 1985; Lockhart and Manders, 1986).

[c]The compound has been labelled in the original reference as in parentheses.

The chemical formula of the compounds was not written in Table 1, except for those synthesised in this work.

References: (a) Ramirez-Jimenez et al., 2009; (b) Kobakhidze et al., 2010; (c) Camacho-Camacho et al., 2009; (d) Esparza-Ruiz et al., 2009; (e) Bordinhao et al., 2006.

suggests the bis(pyrimidin-2-ylthio)alkanes as labile ligands upon coordination. Dissociation of bis(pyridin-2-ylthio)alkanes in solvents such as methanol, acetonitrile and water has been reported before on green copper(II) clusters. Suitable crystals for X-ray diffraction studies from these copper(II) derivatives have been obtained, although it is not clear how the technique works for achieving crystallisation (Samanamu et al., 2008). No ^{119}Sn NMR has been carried out for complexes **11** and **13** due to technical reasons, but it is assumed that they have the same geometrical pattern as for the organotin(IV) derivatives of the corresponding metal precursor.

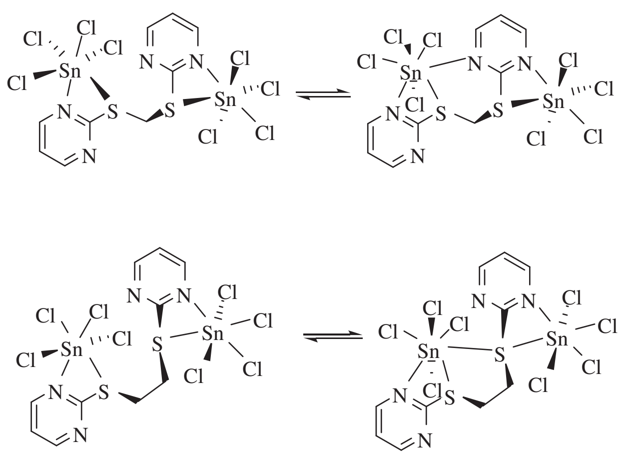

Figure 3 Chemical equilibrium involving [Sn_2Cl_8(*ptm*)]·H_2O (**4**) and [Sn_2Cl_8(*pte*)] (**8**).

Gel permeation chromatography (GPC)

GPC was used herein to gain information on the molar mass of organotin(IV) compounds. The GPC analysis in DMF displayed approximately a mean molecular mass of 1.8×10^{3} g/mol. In view of this, these organotin derivatives of bis(pyrimidin-2-ylthio)alkanes are certainly not polymeric materials. Two peaks in **9** indicate a mixture of compounds in DMF. In **6** and **11**, the mean molecular mass was approximately three or four times the calculated molecular mass. In view of this, decomposition, autoassociation or formation of dimers and trimers are likely in DMF.

Conclusions

The bis(pyrimidin-2-ylthio)alkanes are acting as bridging-mono- and bridging-bidentate ligands towards the tin(IV) nucleus, leading to two geometric patterns, a trigonal-bipyramidal and an octahedral one.

Experimental

Experiments of ^{1}H, ^{13}C and ^{119}Sn NMR were performed using a Varian-Mercury-300 and a Bruker DPX-400 spectrometer equipped with an 89 mm wide-bore magnet. Tetramethylsilane ($SiMe_4$) and tetramethyltin ($SnMe_4$) were used as internal standard (δ=0). Infrared spectra were recorded on a Perkin-Elmer FT-IR 1000 spectrometer, using Nujol suspension between CsI windows, scanning from 4000 to 200 cm^{-1}. The molecular mass was obtained by GPC in dimethylformamide (DMF). The data were obtained using a Shimadzu device by means of a GPC803D-GPC802D 2×300×8 mm column. Microanalysis and melting points determinations were carried out by a Perkin-Elmer 2400 CHN analyser and a digital apparatus MQAPF-301, respectively. Vacuum techniques, dry nitrogen atmosphere and Schlenk glassware were used throughout the experimental work.

Preparation of bis(pyrimidin-2-ylthio)alkanes and organotin adducts

The bis(pyrimidin-2-ylthio)alkanes were synthesised following the experimental method outlined in the literature (de Castro et al., 2002). These ligands were purified from a dichloromethane solution. Solid product was separated after evaporating the solvent until one-third was left, which was filtered off in air and kept in a desiccant container. The organotin(IV) compounds were prepared according to the experimental procedure reported for pyridinethiolalkanes, with slight modifications (Pellei et al., 2006).

Bis(pyrimidin-2-ylthio)alkanes

Bis(pyrimidin-2-ylthio)methane (*ptm*) Yield: 1.51 g (34%). Yellow-green solid; Mp (°C) 150–151; microanalysis required for $C_9H_8N_4S_2$: C, 45.74; H, 3.41; N, 23.71. Found: C, 45.64; H, 3.41; N, 23.12. IR (Nujol/CsI): 1563, 1547 (C=N+C=C), ^{1}H NMR (CDCl$_3$, 300 MHz; δ, ppm; d, doublet; t, triplet; m, multiplet): δ 4.92 (s, S-CH$_2$, 2H), 7.00 (t, pym, 2H), 8.55 (d, pym, 4H). ^{13}C NMR (CDCl$_3$, 75.4 MHz): δ 33.0 (S-CH$_2$), δ 117.1, 157.6, 171.5 (pym).

1,2-Bis(pyrimidin-2-ylthio)ethane (*pte*) Yield: 1.96 g (40%). Pale-orange solid; Mp (°C) 144–145; microanalysis required for $C_{10}H_{10}N_4S_2$: C, 47.98; H, 4.03; N, 22.38. Found: C, 47.26; H, 4.09; N, 21.67. IR (Nujol/CsI): 1564, 1546 (C=N+C=C), ^{1}H NMR (CDCl$_3$, 300 MHz; δ, ppm; d, doublet; t, triplet; m, multiplet): δ 3.51 (s, S-CH$_2$, 4H), 6.73 (t, pym, 2H), 8.51 (d, pym, 4H). ^{13}C NMR (CDCl$_3$, 75.4 MHz): δ 30.7 (S-CH$_2$), 116.9, 157.6, 172.2 (pym).

1,6-Bis(pyrimidin-2-ylthio)hexane (*pth*) Yield: 2.33 g (51%). Yellow solid; Mp (°C) 57–58; microanalysis required for $C_{14}H_{18}N_4S_2$: C, 54.87; H, 5.92; N, 18.28. Found: C, 54.69; H, 6.05; N, 18.60. IR (Nujol/CsI): 1561, 1548 (C=N+C=C), ^{1}H NMR (CDCl$_3$, 300 MHz; δ, ppm; d, doublet; t, triplet; m, multiplet): δ 1.49 (m, CH$_2$, 4H), 1.75 (m, CH$_2$, 4H), 3.13 (t, S-CH$_2$, 4H), 6.95 (t, pym, 2H), 8.49 (d, pym, 4H). ^{13}C NMR (CDCl$_3$, 75.4 MHz): δ 28.6 (CH$_2$), 29.2 (CH$_2$), 31.0 (S-CH$_2$), 116.5, 157.4, 172.8 (pym).

Organotin complexes

[$Sn_2Cl_2Ph_6$(*ptm*)] (1) Yield: 0.79 g (74%). Pale-yellow solid; Mp (°C): 94–95; microanalysis required for $C_{45}H_{38}N_4S_2Cl_2Sn_2$: C, 53.66; H, 3.80; N, 5.56. Found: C, 53.53; H, 3.90; N, 5.59; mol. wt. (g/mol): 1.3×10^3. IR (Nujol/CsI): 3050 (Ph), 1564, 1547 (C=N+C=C), 441 (Sn-N), 334 (Sn-Cl), 271 (Sn-C). ^{1}H NMR (CDCl$_3$, 300 MHz; δ, ppm; d, doublet; t, triplet; m, multiplet): δ 4.94 (s, S-CH$_2$, 2H), 7.00 (t, pym, 2H), 7.44–7.69 (m, Ph, 30H), 8.56 (d, pym, 4H). ^{13}C NMR (CDCl$_3$, 100.6 MHz): δ 32.7 (S-CH$_2$), δ 117.0 (pym), 129.1, 130.4, 136.0, 137.2 (Ph), 157.3, 171.3 (pym). ^{119}Sn NMR {CH$_2$Cl$_2$, 149.2 MHz}: δ -46.8.

[$Sn_2Cl_4Ph_4$(*ptm*)] (2) Yield: 0.87 g (89%). Pale-yellow solid; Mp (°C): 103–104; microanalysis required for $C_{33}H_{28}N_4S_2Cl_4Sn_2$: C, 42.90; H, 3.05; N, 6.06. Found: C, 42.30; H, 3.16; N, 6.43; mol. wt. (g/mol): 1.5×10^3. IR (Nujol/CsI): 3058 (Ph), 1567, 1554 (C=N+C=C), 445 (Sn-N), 354, 326 (Sn-Cl), 276 (Sn-C). ^{1}H NMR (CDCl$_3$, 300 MHz; δ, ppm; d, doublet; t, triplet; m, multiplet): δ 4.93 (s, S-CH$_2$, 4H), 7.01 (t, pym, 2H), 7.53–7.72 (m, Ph, 20H), 8.56 (d, pym, 4H). ^{13}C NMR (CDCl$_3$, 100.6 MHz): δ 32.6 (S-CH$_2$), δ 116.7 (pym), 129.6, 131.7, 135.0, 137.2 (Ph), 157.3, 171.1 (pym). ^{119}Sn NMR {CH$_2$Cl$_2$, 149.2 MHz}: δ -38.3.

[$Sn_2Cl_6Ph_2$(*ptm*)]·CH_2Cl_2 (3) Yield: 0.68 g (76%). Yellow solid; Mp (°C): 98–99; microanalysis required for $C_{22}H_{20}N_4S_2Cl_8Sn_2$: C, 28.55; H, 2.18; N, 6.05. Found: C, 27.40; H, 2.35; N, 6.35; mol. wt. (g/mol): 1.3×10^3. IR (Nujol/CsI): 3055 (Ph), 1602, 1568, 1556 (C=N+C=C), 443 (Sn-N), 360 (Sn-S), 322, 314 (Sn-Cl), 279 (Sn-C). ^{1}H NMR (DMSO-d$_6$, 300 MHz; δ, ppm; d, doublet; t, triplet; m, multiplet): δ 4.88 (s, S-CH$_2$, 2H), 7.25–7.36 (m, Ph, 10H), 7.88 (d, pym, 2H), 8.69 (d, pym, 4H). ^{13}C NMR (DMSO-d$_6$, 75.4 MHz): δ 32.5 (S-CH$_2$), δ 118.4 (pym), 128.0, 128.5, 129.0, 135.4 (Ph), 158.7, 170.4 (pym). ^{119}Sn NMR {CH$_3$OH, 149.2 MHz}: δ -168.7.

[Sn_2Cl_8(*ptm*)]·H_2O (4) Yield: 0.80 g (99%). Pale-yellow solid; Mp (°C): 181–182; microanalysis required for $C_9H_{10}N_4OS_2Cl_8Sn_2$: C, 13.94; H, 1.30; N, 7.23. Found: C, 14.07; H, 1.16; N, 7.23; mol. wt. (g/mol): 1.4×10^3. IR (Nujol/CsI): 3070 (Ph), 1601, 1578 (C=N+C=C), 466 (Sn-N), 384 (Sn-S), 304, 294 (Sn-Cl). ^{1}H NMR (DMSO-d$_6$, 300 MHz; δ, ppm; d, doublet; t, triplet; m, multiplet): δ 4.87 (s, S-CH$_2$, 2H), 7.27 (t, pym, 2H), 8.68 (d, pym, 4H). ^{13}C NMR (DMSO-d$_6$, 75.4 MHz): δ 32.5 (S-CH$_2$), δ 118.4, 158.8, 170.4 (pym). ^{119}Sn NMR {CH$_3$CN, 149.2 MHz}: δ -638.3, -674.6.

[$Sn_2Cl_2Ph_6$(*pte*)] (5) Yield: 0.92 g (90%). Brownish solid; Mp (°C): 97–98; microanalysis required for $C_{46}H_{40}N_4S_2Cl_2Sn_2$: C, 54.10; H, 3.95; N, 5.48. Found: C, 53.98; H, 4.03; N, 5.00; mol. wt. (g/mol): 1.5×10^3. IR (Nujol/CsI): 3065 (Ph), 1563, 1546 (C=N+C=C), 447 (Sn-N), 335 (Sn-Cl), 271 (Sn-C). ^{1}H NMR (CDCl$_3$, 300 MHz; δ, ppm; d, doublet; t, triplet; m, multiplet): δ 3.53 (s, S-CH$_2$, 4H), 6.98 (t, pym, 2H), 7.45–7.70 (m, Ph, 30H), 8.53 (d, pym, 4H). ^{13}C NMR (CDCl$_3$, 100.6 MHz): δ 31.2 (S-CH$_2$), δ 116.6 (pym), 129.1, 130.4, 136.0, 137.2 (Ph), 157.2, 171.8 (pym). ^{119}Sn NMR {CH$_3$CN, 149.2 MHz}: δ -48.0.

[$Sn_2Cl_4Ph_4$(*pte*)] (6) Yield: 0.25 g (27%). Fairly brown solid; Mp (°C): 171 d; microanalysis required for $C_{34}H_{30}N_4S_2Cl_4Sn_2$: C, 43.54; H, 3.22; N, 5.97. Found: C, 43.53; H, 3.20; N, 5.94; mol. wt. (g/mol): 3.6×10^3. IR (CsI): 1604, 1564, 1547 (C=N+C=C), 471 (Sn-N), 451 (Sn-S), 358 (Sn-Cl), 280 (Sn-C).

[$Sn_2Cl_6Ph_2$(*pte*)] (7) Yield: 0.78 g (92%). Pale yellow solid; Mp (°C): 263 d; microanalysis required for $C_{22}H_{20}N_4S_2Cl_6Sn_2$: C, 30.92; H, 2.36; N, 6.56. Found: C, 30.58; H, 2.32; N, 6.50; mol. wt. (g/mol): 1.5×10^3. IR (Nujol/CsI): 3071 (Ph), 1599, 1579 (C=N+C=C), 465 (Sn-N), 381 (Sn-S), 309, 325 (Sn-Cl), 288 (Sn-C). ^{1}H NMR (DMSO-d$_6$, 300 MHz; δ, ppm; d, doublet; t, triplet; m, multiplet): δ 3.47 (s, S-CH$_2$, 4H), 7.20–7.34 (m, Ph, 10H), 7.89 (q, pym, 2H), 8.63 (d, pym, 4H). ^{13}C NMR (DMSO-d$_6$, 75.4 MHz): δ 30.4 (S-CH$_2$), 118.1 (pym), 127.8, 128.3, 135.4, (Ph), 158.6, 171.0 (pym). ^{119}Sn NMR {DMSO, 149.2 MHz}: δ -510.1, -625.2, -632.5, -668.7.

[Sn_2Cl_8(*pte*)] (8) Yield: 0.57 g (95%). Pale-yellow solid; Mp (°C): 182 d; microanalysis required for $C_{10}H_{10}N_4S_2Cl_8Sn_2$: C, 15.57; H, 1.31; N, 7.26. Found: C, 15.39; H, 1.46; N, 7.03; mol. wt. (g/mol): 1.3×10^3. IR (Nujol/CsI): 3073 (Ph), 1599, 1580 (C=N+C=C), 465 (Sn-N), 381 (Sn-S), 311, 284 (Sn-Cl). ^{1}H NMR (DMSO-d$_6$, 300 MHz; δ, ppm; d, doublet; t, triplet; m, multiplet): δ 3.44 (s, S-CH$_2$, 4H), 7.22 (t, pym, 2H), 8.62 (t, pym, 4H). ^{13}C NMR (DMSO-d$_6$, 75.4 MHz): δ 30.5 (S-CH$_2$), 118.1, 158.6, 171.0 (pym). ^{119}Sn NMR {CH$_3$CN, 149.2 MHz}: δ -617.9, -638.7, -675.1.

[SnClPh$_3$(*pth*)] (9) Yield: 0.62 g (90%). Yellow solid; Mp (°C): 47–48. Microanalysis required for $C_{32}H_{33}N_4S_2ClSn$: C, 55.55; H, 4.81; N, 8.10. Found: C, 55.29; H, 5.06; N, 7.99; mol. wt. (g/mol): 1.3×10^3 and 3.7×10^3. IR (CsI): 3060 (Ph), 2933, 2859 (CH_2), 1565, 1548 (C=N+C=C), 465 (Sn-N), 335 (Sn-Cl), 275 (Sn-C). ^{1}H NMR ($CDCl_3$, 300 MHz; δ, ppm; d, doublet; t, triplet; m, multiplet): δ 1.52 (m, CH_2, 4H), 1.75 (m, CH_2, 4H), 3.14 (t, S-CH_2, 4H), 6.94 (t, pym, 2H), 7.44–7.68 (m, Ph, 15H), 8.49 (d, pym, 4H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 28.8 (CH_2), 29.4 (CH_2), 30.9 (S-CH_2), 116.7 (pym), 129.5, 130.9, 136.5, 137.7 (Ph), 157.5, 173.1 (pym). ^{119}Sn NMR {CH_2Cl_2, 149.2 MHz}: δ -51.3.

[Sn$_2$Cl$_2$Ph$_6$(*pth*)] (10) Yield: 0.82 g (93%). Yellow solid; Mp (°C): 50–51. Microanalysis required for $C_{50}H_{48}N_4S_2Cl_2Sn_2$: C, 55.74; H, 4.49; N, 5.20. Found: C, 55.31; H, 4.80; N, 5.76; mol. wt. (g/mol): 1.2×10^3. IR (Nujol/CsI): 1562, 1548 (C=N+C=C), 442 (Sn-N), 335 (Sn-Cl), 272 (Sn-C). ^{1}H NMR ($CDCl_3$, 75.4 MHz; δ, ppm; d, doublet; t, triplet; m, multiplet): δ 1.51 (m, CH_2, 4H), 1.75 (m, CH_2, 4H), 3.15 (t, S-CH_2, 4H), 6.95 (t, pym, 2H), 7.45–7.69 (m, Ph, 30H), 8.50 (d, pym, 4H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 28.1 (CH_2), 28.8 (CH_2), 30.9 (S-CH_2), 116.4 (pym), 129.3, 130.6, 136.2, 137.4 (Ph), 157.2, 172.9 (pym). ^{119}Sn NMR {CH_2Cl_2, 149.2 MHz}: δ -47.1.

[Sn$_2$Cl$_4$Ph$_4$(*pth*)] (11) Yield: 0.59 g (73%). Light-red solid; Mp (°C): 242 d. Microanalysis required for $C_{38}H_{38}N_4S_2Cl_4Sn_2$: C, 45.91; H, 3.85; N, 5.64. Found: C, 46.00; H, 3.85; N, 5.61; mol. wt. (g/mol): 2.9×10^3. IR (CsI): 3048 (Ph), 1610, 1592 (C=N+C=C), 454 (Sn-N), 408 (Sn-S), 308 (Sn-Cl), 259 (Sn-C). ^{1}H NMR (DMSO-d_6, 400 MHz; δ, ppm; d, doublet; t, triplet; m, multiplet): δ 1.43 (m, CH_2, 4H), 1.66 (m, CH_2, 4H), 3.10 (t, S-CH_2, 4H), 7.17–7.38 (m, Ph, 20H), 7.94 (d, pym, 2H), 8.60 (d, pym, 4H). ^{13}C NMR (DMSO-d_6, 100.6 MHz): δ 27.7 (CH_2), 28.6 (CH_2), 29.8 (S-CH_2), 117.0 (pym), 127.6, 127.1, 133.1 (Ph), 157.7, 171.1 (pym).

[Sn$_2$Cl$_6$Ph$_2$(*pth*)] (12) Yield: 0.42 g (56%). Yellow solid; Mp (°C): 116–117. Microanalysis required for $C_{26}H_{28}N_4S_2Cl_6Sn_2$: C, 34.29; H, 3.10; N, 6.15. Found: C, 34.24; H, 3.13; N, 6.15. IR (Nujol/CsI): 1608, 1594 (C=N+C=C), 458 (Sn-N), 358 (Sn-S), 328, 314 (Sn-Cl), 279 (Sn-C). ^{1}H NMR (DMSO-d_6, 300 MHz; δ, ppm; d, doublet; t, triplet; m, multiplet): δ 1.40 (m, CH_2, 4H), 1.64 (m, CH_2, 4H), 3.07 (t, S-CH_2, 4H), 7.15–7.29 (m, Ph, 10H), 7.92 (d, pym, 2H), 8.59 (d, pym, 4H). ^{13}C NMR (DMSO-d_6, 75.4 MHz): δ 28.4 (CH_2), 29.3 (CH_2), 30.5 (S-CH_2), 117.7 (pym), 127.8, 128.1, 135.4, (Ph), 158.4, 171.5 (pym). ^{119}Sn NMR {DMSO-d_6, 74.6 MHz}: δ -669.2, -399.2.

[Sn$_2$Cl$_8$(*pth*)] (13) Yield: 0.35 g (56%). Yellow solid; Mp (°C): 155–156. Microanalysis required for $C_{14}H_{18}N_4S_2Cl_8Sn_2$: C, 20.32; H, 2.19; N, 6.77. Found: C, 20.45; H, 2.10; N, 6.51. IR (CsI): 1601, 1566, 1548 (C=N+C=C), 470 (Sn-N), 309 (Sn-Cl). ^{1}H NMR (DMSO-d_6, 400 MHz; δ, ppm; d, doublet; t, triplet; m, multiplet): δ 1.43 (m, CH_2, 4H), 1.65 (m, CH_2, 4H), 3.10 (t, S-CH_2, 4H), 7.19 (t, pym, 2H), 8.62 (d, pym, 4H). ^{13}C NMR (DMSO-d_6, 100.6 MHz): δ 27.7 (CH_2), 28.6 (CH_2), 29.8 (S-CH_2), 117.0, 157.6, 171.1 (pym).

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References

Adhikary, B.; Lucas, C. R. Copper(II) complexes of N2S3 ligands involving aromatic nitrogen and thioether donors and having high redox potentials. *Inorg. Chem.* **1994**, *33*, 1376–1381.

Alallaf, T. A. K. C-13 NMR-studies of some organotin(IV) compounds. *J. Organomet. Chem.* **1986**, *306*, 337–346.

Amoedo-Portela, A.; Carballo, R.; Casas, J. S.; Garcia-Martinez, E.; Sanchez-Gonzalez, A.; Sordo, J.; Vazquez-Lopez, E. M. Bis(2-pyridylthio)methane complexes of cadmium(II) halides. *Polyhedron* **2003**, *22*, 1077–1083.

Barclay, J. E.; Davies, S. C.; Evans, D. J.; Fairhurst, S. A.; Fowler, C.; Henderson, R. A.; Hughes, D. L.; Oglieve, K. E. Transfer of a quadridentate N2S2 ligand from M2+(M=Cr, Mn, Fe, Co or Ni) to Cu2+: unexpected reactivities of bimetallic intermediates. *Transition Met. Chem.* **1998**, *23*, 701–713.

Baul, T. S. B.; Dhar, S.; Pyke, S. M.; Tiekink, E. R. T.; Rivarola, E.; Butcher, R.; Smith, F. E. Synthesis and characterization of triorganotin(IV) complexes of 5-[(E)-2-(aryl)-1-diazenyl]-2-hydroxybenzoic acids. Crystal and molecular structures of a series of triphenyltin 5-[(E)-2-(aryl)-1-diazenyl]-2-hydroxybenzoates (aryl=phenyl, 2-methylphenyl, 3-methylphenyl and 4-methoxyphenyl). *J. Organomet. Chem.* **2001**, *633*, 7–17.

Bordinhao, J.; Comerlato, N. M.; Ferreira, G. B.; Howie, R. A.; da Silva, C. X. A.; Wardell, J. L. 4,5-Bis[(triorganotin)thiolato]-1,3-dithiole-2-thione, (R_3Sn)(2)(dmit), 4,5-bis [(triorganotin) thiolato]-1,3-dithiole-2-one, (R_3Sn)(2)(dmio), compounds: crystal structures of (cyclohexyl(3)Sn)(2)(dmio), (Ph_3Sn)(2)(dmit) and (Ph_3Sn)(2)(dmio). *J. Organomet. Chem.* **2006**, *691*, 1598–1605.

Camacho-Camacho, C.; Esparza-Ruiz, A.; Vasquez-Badillo, A.; Noth, H.; Flores-Parra, A.; Contreras, R. Fused hexacyclic tin compounds derived from 3-(3,5-di-t-butyl-2-hydroxyphenylimino)-3H-phenoxazin-2-ol. *J. Organomet. Chem.* **2009**, *694*, 726–730.

Caruso, F.; Giomini, M.; Giuliani, A. M.; Rivarola, E. Synthesis and spectroscopic studies (Mossbauer, IR and NMR) of [R(2)SnCl(2) bipym] (R=butyl or phenyl) and the crystal and molecular-structure of [Ph(2)SnCl(2)Bipym]. *J. Organomet. Chem.* **1994**, *466*, 69–75.

Casas, J. S.; Sánchez, A.; Sordo, J.; Vázquez-lópez, A.; Castellano, E. E.; Zukerman-Schpector, J.; Rodríguez-Argüelles, M. C.; Russo, U. Diorganotin(IV) derivatives of salicylaldehydethiosemicarbazone. The crystal structure of dimethyl- and diphenyl-(salicylaldehydethiosemicarbazonato)tin(IV). *Inorg. Chim. Acta* **1994**, *216*, 169–175.

Chou, J. L.; Horng, D. N.; Chyn, J. P.; Lee, K. M.; Urbach, F. L.; Lee, G. H.; Tsai, H. L. Dinuclear copper(II) complexes incorporating a new pyrazolo-based sulfur-containing binucleating ligand. *Inorg. Chem. Commun.* **1999**, *2*, 392–395.

de Castro, V. D.; de Lima, G. M.; Filgueiras, C. A. L.; Gambardella, M. T. P. The molecular structure and spectral studies of mercaptopyridyl-based ligands. *J. Mol. Struct*. **2002**, *609*, 199–203.

de Mello, V. J.; Maia, J. R. D.; de Oliveira, T. T.; Nagem, T. J.; Ardisson, J. D.; Patricio, P. S. D.; de Lima, G. M. Tin(IV) compounds derivatives of reaction between organotin(IV), $SnCl_4$ and rutin trihydrate: characterization and hypolipidemic effects. *Main Group Met. Chem*. **2004**, *27*, 309–321.

Domazetis, G.; Magee, R. J.; James, B. D.; Cashion, J. D. Synthesis and spectroscopic studies of organotin compounds containing the Sn-S bond. *J. Inorg. Nucl. Chem.* **1981**, *43*, 1351–1359.

Esparza-Ruiz, A.; Pena-Hueso, A.; Ramos-Garcia, I.; Vasquez-Badillo, A.; Flores-Parra, A.; Contreras, R. Hypervalent triphenyl and diphenyl tin coordination compounds derived from

2-(1H-benzimidazol-2-yl)phenol. *J. Organomet. Chem.* **2009**, *694*, 269–277.

Gielen, M. Tin-based antitumour drugs. *Coord. Chem. Rev.* **1996**, *151*, 41–51.

Gielen, M. An overview of forty years organotin chemistry developed at the Free Universities of Brussels ULB and VUB. *J. Braz. Chem. Soc.* **2003**, *14*, 870–877.

Gielen, M.; Dalil, H.; Biesemans, M.; Mahieu, B.; de Vos, D.; Willem, R. Di- and tri-organotin derivatives of 3S,4S-3-[(R)-1-(tert-butyl-dimethylsilyloxy)ethyl]-4-[(R)-carboxyethyl]-2-azetidinone: synthesis, characterization and in vitro antitumour activity. *Appl. Organomet. Chem.* **1999**, *13*, 515–520.

Gielen, M.; Biesemans, M.; Willem, R. Organotin compounds: from kinetics to stereochemistry and antitumour activities. *Appl. Organomet. Chem.* **2005**, *19*, 440–450.

Gómez, E.; Flores, R.; Huerta, G.; Alvarez-Toledano, C.; Toscano, R. A.; Santes, V.; Nava, N.; Sharma, P. Dimethyltin(IV) 2,6-disubstituted pyridine complexes. *J. Organomet. chem.* **2003**, *672*, 115–122.

Handlir, K.; Holecek, J.; Nadvornik, M.; Teleb, S. M.; Lycka, A. Sn-119 and C-13 NMR – study of some trivinyltin(IV) compounds and their complexes. *Inorg. Chim. Acta* **1988**, *150*, 287–291.

Hani, R.; Geanangel, R. A. 119Sn NMR in coordination chemistry. *Coord. Chem. Rev.* **1982**, *44*, 229–246.

Holecek, J.; Nádvorník, M.; Handlir, K.; Lycka, A. 13C and 119Sn NMR study of some four- and five-coordinate triphenyltin(IV) compounds. *J. Organomet. Chem.* **1983**, *241*, 177–184.

Kinoshita, I.; Wright, L. J.; Kubo, S.; Kimura, K.; Sakata, A.; Yano, T.; Miyamoto, R.; Nishioka, T.; Isobe, K. Design and synthesis of copper complexes of novel ligands based on the pyridine thiolate group. *Dalton Trans.* **2003**, 1993–2003.

Kobakhidze, N.; Farfan, N.; Romero, M.; Manuel Mendez-Stivalet, J.; Gabriela Ballinas-Lopez, M.; Garcia-Ortega, H.; Dominguez, O.; Santillan, R.; Sanchez-Bartez, F.; Gracia-Mora, I. New pentacoordinated Schiff-base diorganotin(IV) complexes derived from nonpolar side chain α-amino acids. *J. Organomet. Chem.* **2010**, *695*, 1189–1199.

Lockhart, T. P.; Manders, W. F. Structure determination by NMR-sepectroscopy – correlation of [2J(Sn-119,H-1) and the Me-Sn-Me angle in methyltin(IV) compounds. *Inorg. Chem.* **1986**, *25*, 892–895.

Lockhart, T. P.; Manders, W. F.; Zuckerman, J. J. Structural investigations by solid-state C-13 NMR – dependence of [1J(Sn-119,C-13)] on the Me-Sn-Me angle in methyltin(IV)s. *J. Am. Chem. Soc.* **1985**, *107*, 4546–4547.

Ma, C. L.; Tian, G. R.; Zhang, R. F. New triorganotin(IV) complexes of polyfunctional S,N,O-ligands: supramolecular structures based on pi center dot center dot center dot pi C-H center dot center dot center dot pi interactions. *J. Organomet. Chem.* **2006**, *691*, 2014–2022.

Mathiasch, B. Carbon-13 NMR parameters of phenyltin halogenides and phenyltin chalcogenides. *Org. Magn. Reson.* **1981**, *17*, 296–298.

Matthews, C. J.; Clegg, W.; Heath, S. L.; Martin, N. C.; Hill, M. N. S.; Lockhart, J. C. Coordination of Zn(II), Cd(II), Hg(II), and Ag(I) by bis(benzimidazole) ligands. *Inorg. Chem.* **1998**, *37*, 199–207.

Miyamoto, R.; Santo, R.; Matsushita, T.; Nishioka, T.; Ichimura, A.; Teki, Y.; Kinoshita, I. A complete series of copper(II) halide complexes (X=F, Cl, Br, I) with a novel Cu(II)-C(sp(3)) bond. *Dalton Trans.* **2005**, 3179–3186.

Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds Part B: Applications in Coordination, Organometallic, and Bioinorganic Chemistry*; 5th edition. John Wiley & Sons Inc.: New York, 1997.

Otera, J. ^{119}Sn chemical shifts in five- and six-coordinate organotin chelates. *J. Organomet. Chem.* **1981**, *221*, 57–61.

Otera, J.; Kusaba, A.; Hinoishi, T. Studies on ^{119}Sn and ^{207}Pb NMR spectra of seven-coordinate organo-tin and -lead chelates. *J. Organomet. Chem.* **1982**, *228*, 223–228.

Pellei, M.; Lobbia, G. G.; Mancini, M.; Spagna, R.; Santini, C. Synthesis and characterization of new organotin(IV) complexes with polyfunctional ligands. *J. Organomet. Chem.* **2006**, *691*, 1615–1621.

Ramirez-Jimenez, A.; Gomez, E.; Hernandez, S. Penta- and heptacoordinated tin(IV) compounds derived from pyridine Schiff bases and 2-pyridine carboxylate: synthesis and structural characterization. *J. Organomet. Chem.* **2009**, *694*, 2965–2975.

Samanamu, C. R.; Lococo, P. M.; Woodul, W. D.; Richards, A. F. Copper halide clusters and polymers supported by bipodal heteroelemental ligands. *Polyhedron* **2008**, *27*, 1463–1470.

Singh, N. K.; Sharma, U.; Kulshreshtha, S. K. Synthesis and spectral characterization of diorganotin(IV) complexes of thiohydrazides ang thiohydrazone. *J. Organomet. Chem.* **1990**, *382*, 375–381.

Tarassoli, A.; Asadi, A.; Hitchcock, P. B. Synthesis and crystal structures of new complexes of di- and tribenzyltin 2-amino-1-cyclopentene-1-carbodithioates. *J. Organomet. Chem.* **2006**, *691*, 1631–1636.

Von Poelhsitz, G.; de Araujo, M. P.; de Oliveira, L. A. A.; Queiroz, S. L.; Ellena, J.; Castellano, E. E.; Ferreira, A. G.; Batista, A. A. fac-[RuCl$_3$(NO)(dppb)] (I) and mer-[RuCl$_3$(NO)(diop)] (II) complexes: syntheses, characterization and X-ray structures. *Polyhedron* **2002**, *21*, 2221–2225.