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Synthesis, structural characterization and crystal structure of some dimethyltin complexes containing substituted 1,10-phenanthroline

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ABSTRACT

The reaction of dimethyltin dichloride with four substituted 1, 10- phenanthroline has been studied. The reactions of dimethyltin dichloride with 5-methyl-1,10-phenanthroline (Mephen); 5,6-dimethyl-1,10-phenanthroline (Me_2phen); 5-nitro-1,10-phenanthroline (NO_2phen); 5-chloro-1,10-phenanthroline (Clphen) resulted in the formation of the hexa-coordinated complexes of [$SnMe_2Cl_2$(NN)] {Mephen (**1**), Me_2phen (**2**), NO_2phen (**3**), Clphen (**4**)}. The resulting products have been fully characterized by elemental analysis, multinuclear (^{1}H, ^{13}C, ^{119}Sn) NMR, DEPT-135, HHCOSY and HSQC NMR spectroscopy. The solid state X-ray determination of complexes [$SnMe_2Cl_2$(Mephen)] (**1**) and [$SnMe_2Cl_2$(Me_2phen)] (**2**) revealed that the complexes **1** and **2** contain the hexa-coordinated tin(IV) atom in an octahedral geometry with the *trans*-[$SnMe_2$] configuration. The Sn–N bond distances in **1**–**2** are 2.47–2.48 Å which are almost among the largest values.

1. Introduction

The various derivatives of organotin compounds such as diimines, terpyridines or carboxylates display potential applications such as a variety of biological activities, particularly, antibacterial, anti-tumour and anti-cancer activity [1–8]. Three factors of organic group R, the halide or pseudohalide and the nature of donor ligand are important in the activity of organotin compounds. For example, most dibromo complexes are active than the corresponding dichloro or diiodo analogues. The majority of the investigation of the activity of the organotin complexes has been focused on the bidentate ligand with *cis*-halogens, since they are structurally similar to those of active platinum complexes [9]. For example, [$SnEt_2Cl_2$(phen)] (phen = 1,10-phenanthroline) containing *cis*-Cl_2 as a leaving group, can intercalate into DNA, resulting in the unwinding of the DNA or interacts with DNA by ion binding or hydrophobic interacting which stabilize the metal complex-DNA system [1]. It has been shown that the active Sn(IV) complexes containing N-donor atoms have the average Sn–N bond lengths > 2.39 Å which reveals the pre-dissociation of the ligand as an important step in these complexes [10].

The use of chelating pyridyl ligand in the coordination chemistry of tin adducts has grown rapidly, with the various substituted 2,2'-bipyridine and 1,10-phenanthroline as the bidentate ligands [11–16]. The *trans*-configuration of R_2 have been observed in [SnR_2Cl_2(phen)] {R = *p*-Clbenzyl, *p*-methylbenzyl, benzyl) [17–19]. The unusual feature of *cis*-[$SnPh_2$] configuration in [$SnPh_2Cl_2$(bu_2bpy)] (bu_2bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) has been assigned to the steric hindrance between bu_2bpy group and phenyl group on the tin atom [16]. On the other hand, *trans*-[$SnMe_2$] and *trans*-[$SnCl_2$] configurations in [$SnMe_2Cl_2$(bupy)] (bupy = 4-*tert*-butylpyridine) was observed which differs from *cis*-[$SnCl_2$] configuration in the corresponding diimine ligand of bu_2bpy [16].

In spite of the well-known chemistry of organotin complexes, the variety of structures containing the phenanthroline ligand is more diverse than those of substituted phenanthroline ligands [20]. For example, *trans*-configuration of phenyl groups in [$SnPh_2Cl_2$(5-Mephen)] and [$SnPh_2Cl_2$(4,7-Me_2phen)] has been known [21]. *Trans*- or distorted *trans*-[SnR_2] configuration were observed for the dialkyltin dihalide complexes [22,23].

The functionalization of the phenanthroline moiety enables the formation of the complexes which change the spectroscopic and electronic properties of the products and therefore, broadening the potential application for the biological studies. Herein, we report on the preparation, NMR data and crystal structures of new organotin(IV) complexes containing a series of the substituted chelating ligand of 1,10-phenanthroline to provide more information about

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their structural properties. Four different types of substituted phenanthroline were examined (5-methyl, 5,6-dimethyl, 5-NO_2 and 5-Cl) that ranged from electron-donating to electron-withdrawing, as shown in Scheme 1.

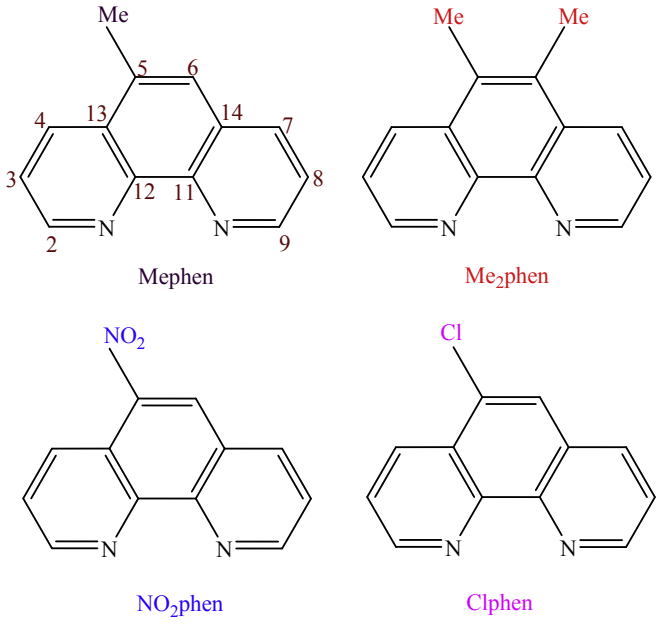
2. Experimental

2.1. General remarks

Elemental analyses were performed on a Costech ECS 4010 elemental analyzer. The ^{1}H, ^{13}C, ^{119}Sn, HH-COSY, HSQC and DEPT-135 NMR spectra were recorded using Bruker DPX 300 and Bio-spin GmbH 400 spectrometers. All the chemical shifts and coupling constants are reported in ppm and Hz, respectively. The ^{1}H, ^{13}C and ^{119}Sn NMR spectra are reported relative to TMS (^{1}H, ^{13}C) and $SnMe_4$ (^{119}Sn).

2.2. Preparation of [$SnMe_2Cl_2$(Mephen)] (**1**)

A solution of Mephen (30 mg, 0.15 mmol) in acetone (5 mL) was added to a solution of $SnMe_2Cl_2$ (34 mg, 0.15 mmol) in diethyl ether (5 mL). The reaction mixture was stirred for 24 h at room temperature. The solvent was removed under reduced pressure and the resulting residue was solidified with dichloromethane/n-hexane to give a white solid. Yield: 54%; m.p. 212–214 °C. Anal. Calc. for $C_{15}H_{16}Cl_2N_2Sn$: C, 43.53; H, 3.90; N, 6.77. Found: C, 43.73; H, 3.99; N, 7.12%. NMR data in $CDCl_3$: $\delta(^{1}H)$ 2.94 [s, 3H, CH_3 of Mephen], 1.12 [s, 6H, $^{2}J(^{119}Sn–H)$ = 113.3, $^{2}J(^{117}Sn–H)$ = 108.5 Hz, Sn–Me]; (Mephen group) 7.95 [s, 1H, H^6], 8.00 [dd, 1H, J = 8.0, 8.0 Hz, H^8], 8.09 [dd, 1H, J = 8.0, 8.0 Hz, H^3], 8.60 [dd, 1H, J = 8.4, 1.6 Hz, H^7], 8.82 [dd, 1H, J = 8.8, 1.6 Hz, H^4], 9.77 [dd, 1H, J = 4.8, 1.6 Hz, H^9], 9.86 [dd, 1H, J = 4.8, 1.6 Hz, H^2]; $\delta(^{13}C)$ 19.4 [s, CH_3 of Mephen], 25.7 [s, $^{1}J(^{119}Sn–C)$ = 1097 Hz, $^{1}J(^{117}Sn–C)$ = 1049 Hz, Sn–Me]; (Mephen group) 125.3 (C_3), 125.5 (C_8), 126.8 (C_6), 130.0 (C_{13}), 130.4 (C_{14}), 135.3 (C_5), 136.7 (C_4), 138.9 (C_{12}), 139.2 (C_7), 139.8 (C_{11}), 147.5 (C_2), 147.9 (C_9); $\delta(^{119}Sn)$ in $CDCl_3$: −262. Crystals suitable for X-ray structure determination were grown from a dichloromethane/n-hexane solution.



Scheme 1.

2.3. Preparation of [$SnMe_2Cl_2$(Me_2phen)], (**2**)

Following the same procedure as the preparation of **1**, this was prepared using Me_2phen (30 mg, 0.14 mmol) and $SnMe_2Cl_2$ (32 mg, 0.14 mmol) to afford a white solid. Yield: 75%; m.p. 258–260 °C (dec). Anal. Calc. for $C_{16}H_{18}Cl_2N_2Sn$: C, 44.91; H, 4.24; N, 6.55. Found: C, 44.06; H, 4.84; N, 6.09%. NMR data in $CDCl_3$: $\delta(^{1}H)$ 2.90 [s, 6H, CH_3 of Me_2phen], 1.11 [s, 6H, $^{2}J(^{119}Sn–H)$ = 110.5 Hz, $^{2}J(^{117}Sn–H)$ = 106.5 Hz, Sn–Me]; (Me_2phen group) 8.05 [dd, 2H, J = 8.8, 8.8 Hz, $H^{3,8}$], 8.87 [dd, 2H, J = 8.8, 1.6 Hz, $H^{4,7}$], 9.81 [dd, 2H, J = 4.8, 1.2 Hz, $H^{2,9}$]; $\delta(^{13}C)$ 15.7 [s, CH_3 of Me_2phen], 25.0 [s, $^{1}J(^{119/117}Sn–C)$ not resolved, Sn–Me]; (Me_2phen group) 125.2 ($C_{3,8}$), 130.4 ($C_{5,6}$), 131.6 ($C_{13,14}$), 136.2 ($C_{4,7}$), 138.8 ($C_{11,12}$), 147.1 ($C_{2,9}$); $\delta(^{119}Sn)$ in $CDCl_3$: −264. Crystals suitable for X-ray structure determination were grown from a dichloromethane/n-hexane solution.

2.4. Preparation of [$SnMe_2Cl_2$(NO_2phen)], (**3**)

This was prepared similarly using NO_2phen (30 mg, 0.13 mmol) and $SnMe_2Cl_2$ (29 mg, 0.13 mmol) to afford a pale yellow solid. Yield: 84%; m.p. 220–224 °C (dec). Anal. Calc. for $C_{14}H_{13}Cl_2N_3O_2Sn$: C, 37.80; H, 2.95; N, 9.45. Found: C, 38.07; H, 3.18; N, 9.62%. NMR data in DMSO-d_6: $\delta(^{1}H)$ 1.04 [s, 6H, $^{2}J(^{119}Sn–H)$ = 114.1, $^{2}J(^{117}Sn–H)$ = 109.3 Hz, Sn–Me]; (NO_2phen group) 7.97 [dd, 1H, J = 8.4, 8.4 Hz, H^8], 8.00 [dd, 1H, J = 8.4, 8.4 Hz, H^3], 8.81 [dd, 1H, J = 8.4, 2.0 Hz, H^7], 8.92 [dd, 1H, J = 8.4, 1.6 Hz, H^4], 9.05 [s, 1H, H^6], 9.28 [dd, 1H, J = 4.4, 1.6 Hz, H^9], 9.30 [dd, 1H, J = 4.4, 1.6 Hz, H^2]; $\delta(^{13}C)$ 23.6 [s, $^{1}J(^{119}Sn–C)$ = 1026 Hz, $^{1}J(^{117}Sn–C)$ = 981 Hz, Sn–Me]; (NO_2phen group) 121.0 (C_{13}), 125.2 (C_8), 125.3 (C_6), 126.2 (C_{14}), 126.6 (C_3), 133.0 (C_4), 139.4 (C_7), 144.3 (C_5), 145.3 (C_{12}), 146.6 (C_{11}), 151.4 (C_2), 153.5 (C_9); $\delta(^{119}Sn)$ in DMSO-d_6: −244.

2.5. Preparation of [$SnMe_2Cl_2$(Clphen)], (**4**)

This was prepared similarly using Clphen (30 mg, 0.14 mmol) and $SnMe_2Cl_2$ (31 mg, 0.14 mmol) to afford a white solid. Yield: 77%; m.p. 231–233 °C. Anal. Calc. for $C_{14}H_{13}Cl_3N_2Sn$: C, 38.72; H, 3.02; N, 6.45. Found: C, 38.56; H, 3.21; N, 6.56%. NMR data in $CDCl_3$: $\delta(^{1}H)$ 1.15 [s, 6H, $^{2}J(^{119}Sn–H)$ = 110.2, $^{2}J(^{117}Sn–H)$ = 105.6 Hz, Sn–Me]; (Clphen group) 8.04 [dd, 1H, J = 8.4, 8.4 Hz, H^8], 8.14 [dd, 1H, J = 8.8, 8.4 Hz, H^3], 8.24 [s, 1H, H^6], 8.60 [dd, 1H, J = 8.0, 1.6 Hz, H^7], 9.07 [dd, 1H, J = 8.4, 1.6 Hz, H^4], 9.80 [dd, 1H, J = 4.8, 1.6 Hz, H^9], 9.88 [dd, 1H, J = 4.8, 1.6 Hz, H^2]; $\delta(^{13}C)$ 25.3 [s, $^{1}J(^{119}Sn–C)$ = 1074 Hz, $^{1}J(^{117}Sn–C)$ = 1044 Hz, Sn–Me]; (Clphen group) 125.9 (C_8), 126.0 (C_3), 126.7 (C_6), 128.4 (C_{13}), 129.6 (C_{14}), 131.7 (C_5), 136.9 (C_4), 138.8 (C_7), 139.1 (C_{12}), 140.7 (C_{11}), 148.8 (C_2), 149.3 (C_9); $\delta(^{119}Sn)$ in $CDCl_3$: −238.

2.6. X-ray crystal structure determination

Crystallographic data for **1**–**2** and were collected on a MAR345 dtb diffractometer equipped with image plate detector using Mo-Kα X-ray radiation. The structure was solved by direct methods using SHELXS-97, and refined using full-matrix least-squares method on F^2, SHELXL-97 [24]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added at ideal positions and refined using a riding model. A summary of the crystal data, experimental details and refinement parameters for **1**–**2** is given in Table 1.

3. Results and discussion

3.1. NMR studies

The reaction of dimethyltin(IV) dichloride with substituted 1,