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Cis- and *trans*-[SnR_2] configurational isomers in diorganotin(IV) complexes containing mono or bidentate N-donor ligands

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ABSTRACT

The reaction of diorganotin(IV) complexes SnR_2Cl_2 (R = Et, Ph) with the bidentate pyridyl ligand of 4,4′-di-*tert*-butyl-2,2′-bipyridine (bu_2bpy) or phendione (phendione = 1,10-phenanthroline-5,6-dione) resulted in the formation of the hexa-coordinated 1:1 adducts of [SnR_2Cl_2(NN] {R = Et, NN = bu_2bpy (**1**); R = Et, NN = phendione (**2**); R = Ph, NN = bu_2bpy (**3**)}. On the other hand, the reaction of $SnPh_2Cl_2$ with the corresponding monodentate ligand of 4-*tert*-butylpyridine (bupy) affords the 1:2 adduct of [$SnPh_2Cl_2(bupy)_2$] (**4**). The solid state X-ray determination of complex [$SnEt_2Cl_2(bu_2bpy)$] (**1**) revealed that the complex **1** contains the hexa- coordinated tin(IV) atom in an octahedral geometry with the *trans*-[$SnEt_2$] configuration while the X-ray crystal structure determination of complex [$SnPh_2Cl_2(bu_2bpy)$] (**3**) reveals that the tin atom is hexa-coordinated in a distorted octahedral geometry with an unusual feature of the *cis*-[$SnPh_2$] configuration. On the other hand, two carbon, two chlorine and two nitrogen atoms from two pyridyl ligands form an octahedral geometry around tin(IV) atom with *trans-C_2*, *trans-N_2* and *trans-Cl_2* configurations in [$SnMe_2Cl_2(bupy)_2$] (**5**). The resulting products have been fully characterized by elemental analysis, multinuclear NMR (^1H, ^{13}C, ^{119}Sn) and ^2D NMR (HH- COSY, ^1H–^{13}C HMQC) spectroscopy.

1. Introduction

The coordination chemistry of diorganotin(IV) acceptors with nitrogen donor atoms have been widely explored, and a large number of the complexes have been characterized structurally in the solid state by X-ray diffraction [1–4]. Pyridyl ligands such as 2,2′(4,4′)-bipyridyl ligands have been used in the preparation of coordination polymers of organotin compounds [5–6]. Such studies are of particular chemical and pharmaceutical interest, since some of these complexes show biological activity [7–9]. There is a relationship between the antitumor activity of organotin(IV) adducts containing N-donor ligands and Sn–N bond length. The active tin compounds have average Sn–N bond lengths more than 2.39 Å [10]. On the other hand, polypyridyl ligands such as 2,2′:6′,2″-terpyridyl moiety react with tin(IV) compounds to give hexa- or hepta- coordinated tin complexes [11–13]. It is well known that the diorganotin dihalides containing monodentate ligands have *cis*- or *trans*-[SnR_2] configuration whereas those with bidentate ligands usually have *cis* configuration. It has been found that *cis*-halogens are necessary for the effectiveness as antitumour activity [14]. Accordingly, few studies have been devoted to date to the case of diorganotin complexes with *cis*-[SnR_2] configuration. For example, the reaction of $SnMe_2Cl_2$ with 2,2′-bipyridine (bpy), 4,4′-di-*tert*-butyl-2,2′-bipyridine (bu_2bpy) or 1,10-phenanthroline-5,6-dione (phendione) affords the hexa-coordinated complexes [$SnMe_2Cl_2$(NN)] (NN = bpy, bu_2bpy, phendione) with the *trans*-[$SnMe_2$] configuration [4,15]. Crystal structure determination of [$SnPh_2Cl_2$(phendione) shows the *trans* configuration of [$SnPh_2$] which has been confirmed by the results obtained from PM3 calculations [16]. Moreover, dibenzyltin(IV) dichloride, ethylphenyltin(IV) dichloride or dibutyltin(IV) dichloride react with 1,10-phenanthroline to afford the octahedral complexes of [SnR_2Cl_2(phen)] {$R_2 = (PhCH_2)_2$, EtPh, Bu_2} with two *trans*-C_2 groups [17–19]. Similarly, *trans*-configuration of [SnR_2] is preferred in the crystal structure of [$SnEt_2Cl_2L$] (L = 2-(2′-pyridyl)quinoxaline) in which L has chelating properties of 2,2′-bipyridine with the bridging properties of quinoxaline [20]. However, *cis*-[SnR_2] is preferred for the diaryltin dithiocyanate complexes due to the steric effects of the thiocyanate groups [3,14]. Notably, [$Sn(4\text{-}ClC_6H_4)_2Cl_2(4,4'\text{-}Me_2bpy)$] is the first example of the isolation of both *cis*- and *trans*-[SnR_2] configurational isomers [21]. The reaction of organotin(IV) compounds with ligand donors depends upon the nature of organic group R on the organotin compounds, nature of donor ligand, donor ratio, halide or pseudohalide, reaction temperature and solvent [22]. Recently, we have found that the reaction of

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dimethyltin dichloride with 4′-substituted terpyridyl ligands depends upon the nature of 4′-substituted terpyridyl ligand in which the anion exists as Cl^- or $SnM_2Cl_3^-$ or both forms [13].

We have now undertaken a study of the synthesis and spectroscopic characterization of some diorganotin(IV) complexes containing the monodentate pyridyl ligand of 4-*tert*-butylpyridine (bupy) and its corresponding chelate ligand of 4,4′-di-*tert*-butyl-2,2′-bipyridine (bu_2bpy) and 1,10-phenanthroline-5,6-dione (phendione) to investigate the donating ability of these ligands towards diorganotin dichlorides (Scheme 1). The resulting products have been fully characterized by elemental analysis, multinuclear NMR (^1H, ^{13}C, ^{119}Sn) and ^2D NMR (HH- COSY, $^1H–^{13}C$ HMQC) spectroscopy. The molecular structures of [$SnEt_2Cl_2(bu_2bpy)$], [$SnPh_2Cl_2(bu_2bpy)$] and [$SnMe_2Cl_2(bupy)_2$] were determined by X-ray crystallography. The structures of resulting products demonstrate that the nature of functional group on the pyridyl ligand and organic group affect on the coordination geometry of organotin(IV) in the solid state.

2. Experimental

2.1. General remarks

All chemicals were reagent grade and were used as received. Elemental analyses were performed by a Perkin-Elmer 2400 II elemental analyzer. NMR data were recorded using Bruker Biospin GmbH 400 and 500 MHz spectrometers. All the chemical shifts and coupling constants are reported in ppm and Hz, respectively. The ^1H, ^{13}C and ^{119}Sn NMR spectra are reported relative to TMS (^1H, ^{13}C), $SnMe_4$ (^{119}Sn). [$SnMe_2Cl_2(bupy)_2$] and phendione were prepared according to the literature [15,23]. Single crystals of [$SnMe_2Cl_2(bupy)_2$] (**5**) suitable for X-ray structure determination were grown from an acetone solution.

2.2. Preparation of [$SnEt_2Cl_2(bu_2bpy)$] (**1**)

A solution of 4,4′-di-tert-butyl-2,2′-bipyridine (54 mg, 0.20 mmol) in diethyl ether (5 mL) was reacted with a solution of $SnEt_2Cl_2$ (50 mg, 0.20 mmol) in diethyl ether (5 mL) to give a white solid. The product was then filtered off and washed with diethyl ether and air dried. Yield: 60%; m.p. 214-215 °C. *Anal.* Calc. for $C_{22}H_{34}Cl_2N_2Sn$: C, 51.20; H, 6.64; N, 5.43. Found: C, 51.21; H, 6.72; N, 5.43%. NMR data in $CDCl_3$: $\delta(^1H)$ 1.50 [s, 18H, ^tBu], 1.03 [t, 6H, $^3J(^{119/117}Sn–H) = 185.0$ Hz, $^3J(HH) = 7.6$ Hz, CH_3], 1.59 [q, 4H, $^2J(^{119}Sn–H) = 110.0$ Hz, $^2J(^{117}Sn–H) = 100.0$ Hz, $^3J(HH) = 7.6$ Hz, CH_2]; (bu_2bpy group) 7.68 [dd, 2H, $^3J(HH) = 5.6$ Hz, $^4J(HH) = 1.6$ Hz, $H^{5,5'}$], 8.22 [s, 2H, $H^{3,3'}$], 9.40 [d, 2H, $^3J(HH) = 5.6$ Hz, $H^{6,6'}$]; $\delta(^{13}C)$ 30.4 [s, terminal C atoms of ^tBu groups], 35.7 [s, central C atoms of ^tBu groups], 35.1 [s, $^1J(^{119}Sn–C) = 1062$ Hz, $^1J(^{117}Sn–C) = 1008$ Hz, CH_2], 10.8 [s, $^2J(^{119/117}Sn–C) = 54$ Hz, CH_3]; (bu_2bpy group) 165.5 (s, C_2), 118.7 (s, C_3), 149.4 (s, C_4), 123.6 [s, C_5], 148.7 (s, C_6); $\delta(^{119}Sn)$ −248 (br).

2.3. Preparation of [$SnEt_2Cl_2$(phendione)] (**2**)

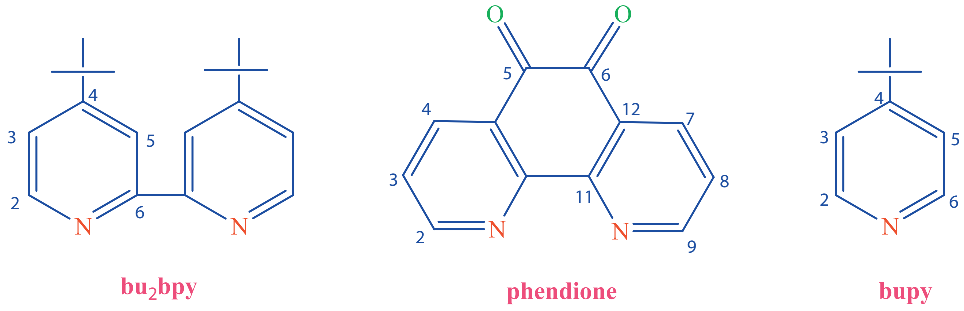
A solution of phendione (74 mg, 0.35 mmol) in dichloromethane (5 mL) was added to a solution of $SnEt_2Cl_2$ (88 mg, 0.35 mmol) in dichloromethane (5 mL). The solution was stirred for 24 h. The solvent was removed under reduced pressure. The resulting yellow residue was recrystallized from dichloromethane/diethyl ether and washed with diethyl ether and air dried. Yield: 55%; m.p. 144–146 °C. *Anal.* Calc. for $C_{16}H_{16}Cl_2N_2O_2Sn$: C, 41.97; H, 3.52; N, 6.12. Found: C, 41.83; H, 3.20; N, 5.97%. NMR data in $CDCl_3$: $\delta(^1H)$ 1.31 [t, 6H, $^3J(^{119}Sn–H) = 160.1$ Hz, $^3J(^{117}Sn–H) = 152.1$ Hz, $^3J(HH) = 8.0$ Hz, CH_3], 1.70 [q, 4H, $^2J(^{119}Sn–H) = 80.0$ Hz, $^2J(^{117}Sn–H) = 72.0$ Hz, $^3J(HH) = 8.0$ Hz, CH_2]; (phendione group) 7.80 [dd, 2H, $^3J(HH) = 7.6$ Hz, $^3J(HH) = 4.8$ Hz, $H^{2,9}$], 8.68 [dd, 2H, $^3J(HH) = 8.0$ Hz, $^4J(HH) = 2.0$ Hz, $H^{3,8}$], 9.40 [dd, 2H, $^3J(HH) = 4.8$ Hz, $^4J(HH) = 1.6$ Hz, $H^{4,7}$]; $\delta(^{13}C)$ 27.0 [s, $^1J(^{119/117}Sn–C)$ not resolved], 10.1 [s, $^2J(^{119/117}Sn–C) = 65$ Hz]; (phendione group) 126.9 (s, C_3), 128.6 (s, C_4), 138.7 (s, C_{12}), 150.6 [s, C_2], 155.4 (s, C_{11}), 177.3 (s, C_5).

2.4. Preparation of [$SnPh_2Cl_2(bu_2bpy)$] (**3**)

A solution of 4,4′-di-*tert*-butyl-2,2′-bipyridine (50 mg, 0.18 mmol) in acetone (5 mL) was added to a solution of $SnPh_2Cl_2$ (50 mg, 0.18 mmol) in acetone (5 mL). The solution was stirred for 24 h. The resultant colorless solution was evaporated to dryness to afford a white solid and then filtered off. The product was then washed with diethyl ether and air dried. Yield: 70%; m.p. 228 °C. *Anal.* Calc. for $C_{30}H_{34}Cl_2N_2Sn$: C, 58.85; H, 5.60; N, 4.58. Found: C, 58.70; H, 5.62; N, 4.47%. NMR data in $CDCl_3$: $\delta(^1H)$ (phenyl groups) 7.39 [m, 2H, $^3J(HH) = 7.2$ Hz, para hydrogens], 7.46 [t, 4H, $^3J(HH) = 7.2$ Hz, meta hydrogens], 8.38 [d, 4H, $^3J(^{119/117}Sn–H) = 89.8$ Hz, $^3J(HH) = 6.8$ Hz, ortho hydrogens]; 1.44 [s, 18H, ^tBu]; (bu_2bpy group) 7.50 [dd, 2H, $^3J(HH) = 6.0$ Hz, $^4J(HH) = 1.2$ Hz, $H^{5,5'}$], 8.27 [s, 2H, $H^{3,3'}$], 8.36 [d, 2H, $^3J(HH) = 6.0$ Hz, $H^{6,6'}$]; $\delta(^{13}C)$ (phenyl groups) 143.4 [s, $^1J(^{119/117}Sn–C)$ not resolved, C_{ipso}], 136.2 [s, $^2J(^{119/117}Sn–C) = 65.4$ Hz, C_{ortho}], 128.4 [s, $^3J(^{119/117}Sn–C) = 90.6$ Hz, C_{meta}], 128.8 [s, $^4J(^{119/117}Sn–C) = 17.1$ Hz, C_{para}]; 30.4 [s, terminal C atoms of ^tBu groups], 35.7 [s, central C atoms of ^tBu groups]; (bu_2bpy group) 166.0 (C_2), 118.4 (C_3), 148.4 (C_4), 124.1 [s, $^3J(^{119/117}Sn–C) = 17.1$ Hz, C_5], 144.8 (s, $^2J(^{119/117}Sn–C) = 31.2$ Hz, C_6); $\delta(^{119}Sn)$ −359 (sh). Crystals suitable for X-ray structure determination were grown from an acetone solution.

2.5. Preparation of [$SnPh_2Cl_2(bupy)_2$] (**4**)

4-*tert*-Butyl pyridine (0.04 mL, 0.26 mmol) was added to a solution of $SnPh_2Cl_2$ (50 mg, 0.14 mmol) in acetone (5 mL). The solution was stirred for 48 h. The solvent was removed under reduced pressure. The resulting residue was recrystallized from acetone/n-hexane and washed with n-hexane and air dried. Yield: 80%; m.p. 145 °C. *Anal.* Calc. for $C_{30}H_{36}Cl_2N_2Sn$: C, 55.04; H, 5.56; N,



Scheme 1.