



Synthesis and structural characterization of dimethyltin(IV) complexes based on functionalized pyridyl ligands

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ABSTRACT

The reaction of dimethyltin dichloride with 1,5-bis(2'-pyridyl)pentane-1,3,5-trione (Htrione) resulted in the formation of the dinuclear complex $\{[\text{Me}_2\text{ClSn}(\mu\text{-trione})\text{SnMe}_2\text{Cl}_2]\cdot\text{Htrione}\}$ (**1**) in the solid state. The solid state X-ray determination of the complex $\{[\text{Me}_2\text{ClSn}(\mu\text{-trione})\text{SnMe}_2\text{Cl}_2]\cdot\text{Htrione}\}$ (**1**) revealed that complex **1** contains the simultaneous presence of penta- and hexacoordinated tin(IV) atoms. Notably, trione acts as a bridging ligand through both oxygen and nitrogen donor atoms. While the hexacoordinated tin(IV) atom adopts an octahedral geometry with a *trans*- $[\text{SnMe}_2]$ configuration, the pentacoordinated tin(IV) atom exists in a highly distorted trigonal bipyramidal arrangement with equatorial methyl groups. It is also important to note that there is a free Htrione molecule as a co-crystal in the di-enol form. The complexes $[\text{SnMe}_2\text{Cl}(\text{tpyCl})]^+[\text{SnMe}_2\text{Cl}_3]^-$ (**2**), $[\text{SnMe}_2\text{Cl}(\text{tpyOH})]^+\text{Cl}^-$ (**3**) and $[\text{SnMe}_2\text{Cl}(\text{tpySH})]^+[\text{SnMe}_2\text{Cl}_3]^-$ (**4**) were also prepared from the reaction of SnMe_2Cl_2 with 4'-functionalized 2,2':6',2''-terpyridines (tpyX), where X = Cl, O, S. It is important to note that the formation of the anion depends upon the nature of 4'-substituted terpyridyl ligand. The resulting products have been fully characterized by IR, elemental analysis and multinuclear (^1H , ^{13}C , ^{119}Sn) NMR spectroscopy. The X-ray crystal structure determination of $[\text{SnMe}_2\text{Cl}(\text{tpyCl})]^+[\text{SnMe}_2\text{Cl}_3]^-$ reveals that the $[\text{SnMe}_2\text{Cl}(\text{tpyCl})]^+$ moiety adopts an octahedral geometry about the tin atom with a *trans* configuration of the methyl ligands. In the $[\text{SnMe}_2\text{Cl}_3]^-$ moiety, the tin(IV) atom exists in a trigonal bipyramidal geometry with equatorial methyl groups.

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1. Introduction

The coordination chemistry of tin(IV) has been demonstrated with several donor ligands such as amines, phosphines, phosphine oxides, arsine oxides, ethers and sulfides [1–6]. Tin(IV) complexes containing diimine and pyridyl ligands, such as 2,2'-bipyridine and 1,10-phenanthroline, have been widely investigated [7–9]. They usually form 1:1 and 1:2 adducts; the resulting adducts usually exist with trigonal bipyramidal or octahedral geometries [1,10]. These complexes play an important role in developing the coordination and organometallic chemistry of tin(IV) compounds [9–11]. There is a relationship between the antitumor activity of organotin(IV) adducts containing N-donor ligands and the Sn–N bond length. Active tin compounds have average Sn–N bond lengths of more than 2.39 Å [12]. Moreover, it has been found that their anti-tumour activities are affected by the nature of the organic group, halide or pseudohalide and the donor ligand [13].

We have recently reported that the reaction of diorganotin(IV) dichlorides $[\text{SnR}_2\text{Cl}_2]$ (R = Me, ⁿBu) with the bidentate pyridyl ligand 1,10-phenanthroline-5,6-dione (phendione) affords the

hexacoordinated 1:1 complexes $[\text{SnR}_2\text{Cl}_2(\text{phendione-}\kappa^2\text{N,N}')]]$, and the basicities towards diorganotin dichlorides vary as expected, N-pyridyl > O donor ligand [14]. In the family of the polypyridine ligands, 2,2':6',2''-terpyridine derivatives are one of the tridentate pyridyl ligands [15]. Terpyridyl complexes have found application in many areas, including biomedicine, catalysis and supramolecular chemistry [16–20]. Up until now, most studies have been devoted to the determination of the crystal structures of tin derivatives containing terpyridyl ligands, whilst their solution chemistry has not yet been investigated. For example, it has been found that tin(IV) compounds react with terpyridyl ligand to form 1:1, 1:2 and 2:3 complexes which depend upon the nature of the halide in the tin(IV) halides, however all of the complexes contain a six-coordinated tin cation [21]. An early report showed that a seven-coordinated dimethyltin(IV) dichloride adduct in a pentagonal bipyramidal geometry was isolated with a tridentate pyridyl heterocycle of 2,4,6-tris(2-pyridyl)-1,3,5-triazine [22]. Furthermore, a seven coordinated dimethyltin(IV) complex, $[\text{SnMe}_2\text{L}]\text{Cl}_2$ (L = N5 donor ligand containing the terpyridyl ligand), has been determined in detail by a single crystal X-ray structure analysis in the reaction of SnMe_2Cl_2 with L [23]. On the other hand, the reaction of SnMe_2Cl_2 with 2,2':6',2''-terpyridine gave $[\text{SnMe}_2\text{Cl}(\text{tpy})]^+[\text{SnMe}_2\text{Cl}_3]^-$, containing a highly distorted octahedral

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environment about the tin(IV) atom in the cation [24]. Interestingly, the reaction of tin(II) chloride with 2,2':6',2''-terpyridine resulted in the formation of the pentacoordinated pseudo-octahedral adduct $[\text{SnCl}_2(\text{tpy})]$, in which the non-bonding electron pair occupied one of the octahedral sites [25]. We report here the synthesis and characterization of a related series of dimethyltin(IV) complexes containing a substituted pyridyl and terpyridyl ligand functionalized in the 4'-position. The resulting products have been fully characterized by IR, elemental analysis, multinuclear (^1H , ^{13}C , ^{119}Sn) NMR spectroscopy and in two cases, by X-ray crystal structures. The resulting products represent new bonding environments for tin which demonstrate that the nature of the functional group on the terpyridyl ligand affects the coordination geometry of tin(IV) in solution as well as the formation of the counterion.

2. Experimental

2.1. General remarks

Diethyl ether was distilled from sodium/benzophenone ketyl and dichloromethane was distilled from P_2O_5 . Elemental analyses were performed on a Perkin-Elmer 2400 II elemental analyzer. IR spectra in the 4000–400 cm^{-1} range were recorded on KBr pellets using an ABB Bomem Model FTLA200-100 spectrophotometer. NMR spectra were recorded using a Bruker Avance DRX 500 MHz spectrometer. All the chemical shifts and coupling constants are reported in ppm and Hz, respectively. The ^1H and ^{13}C NMR spectra are reported relative to TMS (^1H , ^{13}C) and SnMe_4 (^{119}Sn). 4'-Chloro-2,2':6',2''-terpyridine (tpyCl) was purchased from Sigma-Aldrich. 1,5-Bis(2'-pyridyl)pentane-1,3,5-trione (Htrione), 2,2':6',2''-terpyridine-4'(1'H)-one (tpyO) and 2,2':6',2''-terpyridine-4'(1'H)-thione (tpyS) were prepared according to the literature [26,27].

2.2. Preparation of $\{[\text{Me}_2\text{ClSn}(\mu\text{-trione})\text{SnMe}_2\text{Cl}_2]\text{-Htrione}\} (\mathbf{1})$

Htrione (100 mg, 0.37 mmol) was added to a solution of SnMe_2Cl_2 (164 mg, 0.74 mmol) in chloroform (10 mL). The solution color changed from yellow to red and the reaction mixture was stirred for 6 h. The solvent was removed under reduced pressure. The resulting red residue was recrystallized with acetone/diethyl ether, washed with diethyl ether and air-dried. Yield: 37%; M.p. 130 °C (dec). *Anal. Calc.* for $\text{C}_{26.5}\text{H}_{29}\text{Cl}_3\text{N}_3\text{O}_4.5\text{Sn}_2$: C, 39.52; H, 3.63; N, 5.22. Found: C, 39.91; H, 3.30; N, 5.35%. IR data (KBr, cm^{-1}): 3408 (br), 1601 (s), 1577 (s), 1442 (m), 1260 (m), 1211 (m), 1147 (m), 1112 (m), 1083 (m), 1051 (m), 791 (s), 739 (m). NMR data in acetone- d_6 , δ (^1H): 1.20 [s, 12H, 2J ($^{119}\text{Sn-H}$) = 86.9 Hz, 2J ($^{117}\text{Sn-H}$) = 83.5 Hz, Sn-Me], 4.47 [s, 2H, CH_2], 6.93 [br, 1H, OH], 7.01 [s, 1H, CH], 7.57–7.68 [m, 2H, H^3], 8.00–8.13 [m, 4H, $\text{H}^{4,5}$], 8.69–8.77 [m, 2H, H^6]; Resolved ^1H NMR data for free Htrione: 4.52 [s, 2H, CH_2], 7.30 [s, 1H, CH]; δ (^{13}C): 12.6 [s, 1J ($^{119}\text{Sn-C}$) = 655 Hz, 1J ($^{117}\text{Sn-C}$) = 617 Hz, Sn-Me]; trione group: 49.6 [s, CH_2], 99.1 [s, CH], 196.2 [s, C=O]; pyridyl groups: 122.3, 122.4, 122.5, 122.6, 127.3, 127.6, 128.7, 138.3, 138.8, 150.1, 150.3, 151.3, 152.1, 153.4, 172.4, 180.0; Resolved ^{13}C NMR data for free Htrione: 99.0 [s, CH], 195.2 [s, C=O]; δ (^{119}Sn) in acetone- d_6 : 1 (br), -57, -271; in CDCl_3 : -365, -401 (s). Single crystals of $[\text{Me}_2\text{ClSn}(\mu\text{-trione})\text{SnMe}_2\text{Cl}_2]\text{-Htrione}$ (**1**) suitable for X-ray structure determination were grown from an acetone/hexane solution.

2.3. Preparation of $[\text{SnMe}_2\text{Cl}(\text{tpyCl})]^+[\text{SnMe}_2\text{Cl}_3]^- (\mathbf{2})$

A solution of tpyCl (50 mg, 0.19 mmol) in dichloromethane (5 mL) was added to a solution of SnMe_2Cl_2 (41 mg, 0.19 mmol) in dichloromethane (5 mL). The solution was stirred for 24 h,

during which time a white solid formed. The solid was filtered and washed with diethyl ether, and then air dried. Yield: 86%; M.p. 198–199 °C. *Anal. Calc.* for $\text{C}_{19}\text{H}_{22}\text{Cl}_5\text{N}_3\text{Sn}_2$: C, 32.27; H, 3.14; N, 5.94. Found: C, 32.32; H, 2.91; N, 5.98%. IR data (KBr, cm^{-1}): 3066 (m), 2911 (w), 1597 (s), 1559 (s), 1480 (s), 1419 (s), 1250 (m), 1161 (m), 1131 (m), 1018 (s), 803 (s). NMR data in acetone- d_6 , δ (^1H): 1.21 [s, 6H, 2J ($^{119}\text{Sn-H}$) = 86.8 Hz, 2J ($^{117}\text{Sn-H}$) = 83.0 Hz, Sn-Me]; (tpyCl group) 7.55 [ddd, 2H, 3J (HH) = 4.8 Hz, 3J (HH) = 6.1 Hz, 4J (HH) = 1.3 Hz, $\text{H}^{5,5'}$], 8.05 [dt, 2H, 3J (HH) = 7.7 Hz, 4J (HH) = 1.9 Hz, $\text{H}^{4,4'}$], 8.55 [s, 2H, $\text{H}^{3,5'}$], 8.71 [d, 2H, 3J (HH) = 8.0 Hz, $\text{H}^{3,3'}$], 8.79 [d, 2H, 3J (HH) = 4.2 Hz, $\text{H}^{6,6'}$]; δ (^{13}C) in MeOD: 14.1 [s, 1J ($^{119/117}\text{Sn-C}$) = 774 Hz]; tpyCl group: 123.9, 124.3, 127.2, 127.4, 127.6, 131.4, 141.3, 149.8, 152.4; δ (^{119}Sn) in CDCl_3 : -473 (s), 136 (s); in acetone- d_6 : 16 (br); in MeOD: -90 (br). Crystals suitable for X-ray structure determination were grown from an acetone solution.

2.4. Preparation of $[\text{SnMe}_2\text{Cl}(\text{tpyOH})]^+\text{Cl}^- (\mathbf{3})$

Following the same procedure as for the preparation of **2**, a solution of tpyO (113 mg, 0.45 mmol) in dichloromethane (5 mL) was reacted with a solution of SnMe_2Cl_2 (100 mg, 0.45 mmol) in dichloromethane (5 mL) to give a white solid. Yield: 75%; M.p. 153–155 °C. *Anal. Calc.* for $\text{C}_{17}\text{H}_{17}\text{Cl}_2\text{N}_3\text{OSn}$: C, 43.54; H, 3.65; N, 8.96. Found: C, 43.12; H, 3.56; N, 8.93%. IR data (KBr, cm^{-1}): 3260 (m), 3076 (m), 2916 (w), 1590 (s), 1013 (s), 1443 (m), 1363 (m), 793 (m), 738 (w). NMR data in DMSO- d_6 , δ (^1H): 0.99 [s, 6H, 2J ($^{119}\text{Sn-H}$) = 113.1 Hz, 2J ($^{117}\text{Sn-H}$) = 109.5 Hz, Sn-Me], 10.89 [br s, 1H, OH]; (tpyOH group) 7.44 [t, 2H, 3J (HH) = 5.8 Hz, $\text{H}^{5,5'}$], 7.81 [s, 2H, $\text{H}^{3,5'}$], 7.94 [dt, 2H, 3J (HH) = 7.8 Hz, 4J (HH) = 1.4 Hz, $\text{H}^{4,4'}$], 8.54 [d, 2H, 3J (HH) = 7.7 Hz, $\text{H}^{3,3'}$], 8.66 [d, 2H, 3J (HH) = 3.9 Hz, $\text{H}^{6,6'}$]; δ (^{119}Sn) in MeOD: -249 (br), -97 (br).

2.5. Preparation of $[\text{SnMe}_2\text{Cl}(\text{tpySH})]^+_2[\text{SnMe}_2\text{Cl}_3]^- (\mathbf{4})$

Following the same procedure as for the preparation of **2**, a solution of tpyS (52 mg, 0.20 mmol) in dichloromethane (5 mL) was reacted with a solution of SnMe_2Cl_2 (43 mg, 0.20 mmol) in dichloromethane (5 mL) to give a white solid. Yield: 48%; M.p. 236–237 °C. *Anal. Calc.* for $\text{C}_{36}\text{H}_{40}\text{Cl}_6\text{N}_6\text{S}_2\text{Sn}_3$: C, 36.34; H, 3.39; N, 7.06. Found: C, 36.63; H, 3.39; N, 7.06%. IR data (KBr, cm^{-1}): 3059 (m), 2690 (m), 1612 (s), 1576 (s), 1527 (s), 1411 (m), 1343 (w), 1295 (m), 1241 (m), 1001 (m), 788 (s). NMR data in MeOD, δ (^1H): 1.11 [s, 6H, 2J ($^{119}\text{Sn-H}$) = 94.5 Hz, 2J ($^{117}\text{Sn-H}$) = 90.5 Hz, Sn-Me]; (tpySH group) 8.17 [dt, 2H, 3J (HH) = 5.8 Hz, 4J (HH) = 1.1 Hz, $\text{H}^{5,5'}$], 8.71 [dt, 2H, 3J (HH) = 8.0 Hz, 4J (HH) = 1.6 Hz, $\text{H}^{4,4'}$], 8.87 [s, 2H, $\text{H}^{3,5'}$], 8.98 [d, 2H, 3J (HH) = 8.2 Hz, $\text{H}^{3,3'}$], 9.08 [dd, 2H, 3J (HH) = 5.6 Hz, 4J (HH) = 0.95 Hz, $\text{H}^{6,6'}$]; δ (^{13}C) in CDCl_3 : 14.1 [s, 1J ($^{119/117}\text{Sn-C}$) = 464 Hz]; (tpySH group) 123.9, 124.6, 125.6, 126.8, 127.6, 142.5, 145.2, 147.6; δ (^{119}Sn) in DMSO- d_6 : -239 (br); in MeOD: -92 (br).

2.6. X-ray crystal structure determination

All measurements were made on a Bruker APEX DUO diffractometer with graphite monochromated Mo $K\alpha$ radiation. Data for **1** were integrated for both twin components, including both overlapped and non-overlapped reflections. Data were collected and integrated using the Bruker SAINT [28] software packages. Data were corrected for absorption effects using the multi-scan technique (TWINABS [29]), with minimum and maximum transmission coefficients of 0.658 and 0.863, respectively. Data for **2** were corrected for absorption effects using the multi-scan technique (SADABS [30]), with minimum and maximum transmission coefficients of 0.688 and 0.877, respectively. The data were corrected for Lorentz and polarization effects. The structure for **1** was solved by direct

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