

Title: Synthesis, spectroscopic, and structural characterization of new functionalized *gem*-bisphosphonate complexes of tin(IV) chloride

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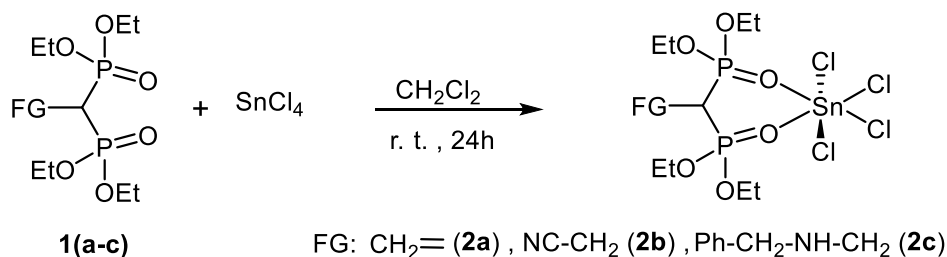
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Abstract

Bisphosphonates of the types X(P(O)(OEt)₂)₂ (X = CH₂=C (**1a**), CNCH₂CH (**1b**) and PhCH₂NCH₂CH (**1c**)) react with SnCl₄ in anhydrous dichloromethane to produce the new tin(IV) adducts [SnCl₄(**1a**)] (**2a**), [SnCl₄(**1b**)] (**2b**) and [SnCl₄(**1c**)] (**2c**) in 72-80% yields. These complexes were characterized using IR, multinuclear (¹H, ¹³C, ³¹P, ¹¹⁹Sn) NMR spectroscopy, elemental analysis, and in one case by single crystal X-ray diffraction. The NMR data show that the bisphosphonate ligands are coordinated to the tin center in a bidentate fashion forming *cis* octahedral tin complexes. Furthermore, the X-ray structure of complex **2b** reveals that the bisphosphonate ligand is coordinated in a bidentate manner to the metal center in a distorted octahedral arrangement with Sn-O-P bond angles in the range 135.95(16)–137.99(18)°. The P=O and Sn-O bond lengths of 1.495(3)-1.497(3) and 2.134(3)-2.146(2) Å, respectively are in the order expected for phosphonate tin(IV) complexes. The results are discussed and compared with closely related analogues.

Graphical abstract



Keywords: *gem*-Bisphosphonates - tin(IV) chloride - ¹¹⁹Sn and ³¹P NMR - X-ray structure.

Specifications Table

Subject area	<i>Organic Chemistry, Crystallography, Spectroscopy</i>
Compounds	<i>gem-bisphosphonate complexes of tin(IV) chloride</i>
Data category	<i>Synthesis, spectral, crystallographic,</i>
Data acquisition format	<i>Multinuclear (^1H, ^{13}C, ^{31}P, ^{119}Sn) NMR spectroscopy, IR, Elemental analysis, Single crystal X-ray diffraction method.</i>
Data type	<i>Process and analysis.</i>
Procedure	<i>New tin(IV) adducts with functionalized gem-bisphosphonate ligands were synthesized and characterized by spectral studies and in the solid state for one case by single crystal X-ray diffraction.</i>
Data accessibility	CCDC-1862268, URL: http://www.ccdc.cam.ac.uk/conts/retrieving .

1. Rationale

The synthesis of bisphosphorylated compounds has attracted an increasing interest over recent years. Such an interest could be explained by the specific properties of bisphosphonate derivatives ranging from pharmacological activities [1-3] to their metal-complexing ability [4-7]. For instance, bisphosphonates have been widely employed in nuclear medicine as ligands for radio-metals in the diagnosis and therapy of several bone diseases, such as osteoporosis and hypercalcemia [8]. Furthermore, it is well established that ligands containing one or more phosphoryl donors form stable complexes with transition metal cations due to their versatile bonding capability. In particular, compounds bearing *gem*-bisphosphonate moieties possess well-known strong chelating properties to form very stable complexes with many metals in a bidentate fashion [9-12]. On the other hand, tin tetrachloride is a strong Lewis acid forming adducts with a variety of neutral ligands [13, 14]. In this context, we have previously reported studies on tin(IV) complexes containing a variety of phosphoryl ligands as Lewis bases, using multinuclear NMR in solution [15-17]. Several factors, such as the nature of substituents on the phosphorus atom, the strength of the Lewis basicity (i.e. the donor character of the P=O group of the ligand) as well as other factors have been shown to influence the structure, properties and stoichiometry of the resulting tin(IV) complexes [15-17]. In our most recent works on phosphonate tin(IV) complexes, we have shown that carbonyl [18] or hydroxy [19] groups do not bind to the tin center in the presence of a phosphonate P=O group and that only the latter is involved in coordination. Herein, we report our results on the synthesis and characterization of SnCl₄ complexes with functionalized *gem*-bisphosphonates containing a nitrogen group in order to explore the binding affinity of such bisphosphonate ligands towards the tin center and to see whether the nitrogen atom could compete with one or both of the ligand P=O groups for metal coordination.

2. Procedure

2.1. Materials and methods

All preparations were carried out under a nitrogen atmosphere in solvent dried by standard technique [20] and stored over molecular sieves. NMR spectra were recorded on a Bruker AC-300 instrument in CDCl₃, CH₂Cl₂ or in a mixture of CDCl₃/DMSO: ^1H NMR spectra were carried out at 300 MHz (TMS), ^{13}C at 75.4 MHz (TMS), ^{31}P at 121 MHz (85% H₃PO₄) and ^{119}Sn at 111.9 MHz (SnCl₄). MAS NMR spectra were recorded on a Bruker AC-300 instrument: ^{119}Sn NMR spectra were obtained at 111.9 MHz (Ph₂SnCl₂). IR spectra were measured on a Perkin-Elmer Paragon 1000 PC spectrometer. The elemental analyses were performed on a SHIMADZU TOC5000A instrument. Tin tetrachloride (Fluka) was used as received.

2.2. General procedure for the synthesis of complexes 2a-c

A solution of *gem*-bisphosphonate (1 mmol) in dry CH₂Cl₂ (5 mL) was slowly added to SnCl₄ (0.26 g, 1 mmol) in the same solvent (20 mL) and the mixture stirred under N₂ for 24 h. The volatiles were then removed *in vacuo* and the residue washed with anhydrous petroleum ether and dried *in vacuo* to give the complexes **2(a-c)** as hygroscopic white solids.

(Tetraethyl ethenylidene-1,1-bisphosphonate)tin(IV) tetrachloride (2a): Yield: 426.16 mg (76%). ¹³C NMR (75 MHz, CDCl₃) δ 16.2, 63.2, 130.3, 149.9. Anal. Calc. for C₁₀H₂₂Cl₄O₆P₂Sn: C, 21.42; H, 3.95 (%). Found: C, 20.91, H, 3.87 (%).

(tetraethyl 2-cyano-ethylidene-1,1-bisphosphonate)tin(IV) tetrachloride (2b): Yield: 423.18 mg (72%). Anal. Calc. for C₁₁H₂₃Cl₄NO₆P₂Sn: C, 22.48; H, 3.94; N, 2.38 (%). Found: C, 23.12; H, 4.05; N, 2.07 (%).

(Tetraethyl 2-benzylamino-ethylidene-1,1-bisphosphonate)tin(IV) tetrachloride (2c): Yield: 534.31 mg (80%). ¹³C NMR (75 MHz, CDCl₃/DMSO) δ 16.3, 25.2, 41.3, 56.9, 60.2, 126.1, 126.75, 127.07, 138.8. Anal. Calc. for C₁₇H₃₁Cl₄NO₆P₂Sn: C, 30.57; H, 4.68; N, 2.10 (%). Found: C, 29.97; H, 4.38; N, 2.51 (%).

2.3. Crystal structure determination

Details of the crystallographic data collection and refinement parameters are presented in Table 1. X-ray diffraction data for compound **2b** was collected at 173 K using a Rigaku SCXmini CCD diffractometer with a SHINE monochromator [Mo K α radiation (λ = 0.71075 Å)]. Intensity data were collected using ω steps accumulating area detector images spanning at least a hemisphere of reciprocal space.

Table 1. Crystal data, data collection and refinement parameters of complex **2b**.

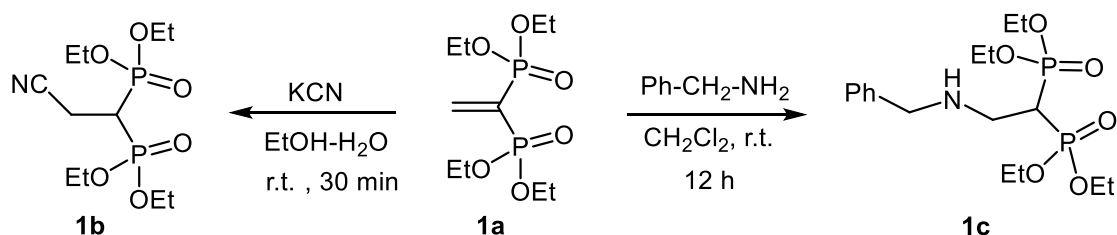
2b	
Compound	[SnCl ₄ (1b) ₂]
Empirical formula	C ₁₁ H ₂₃ Cl ₄ NO ₆ P ₂ Sn
Formula weight (g/mol)	587.76
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁ (#19)
a (Å)	9.4625(6)
b (Å)	14.2940(10)
c (Å)	16.3129(11)
V (Å ³)	2206.4(3)
Z	4
Crystal shape, color	colourless prism
Crystal size (mm)	0.700 x 0.380 x 0.290
Dcalc (g/cm ³)	1.769
Absorption coefficient (mm ⁻¹)	1.811
F (0 0 0)	1168.00
Data	
Goodness-of-fit on F ²	1.050
Final R indices (I > 2 σ (I))	0.0188
R indices (all data)	0.0194
wR2 (all data)	0.0499

All data were corrected for Lorentz polarization effects. A multiscan absorption correction was applied by using CrystalClear [21]. Structures were solved by dual space methods (SHELXT [22]) and refined by full-matrix least-squares against F^2 (SHELXL-2013 [22]).

3. Results and discussion

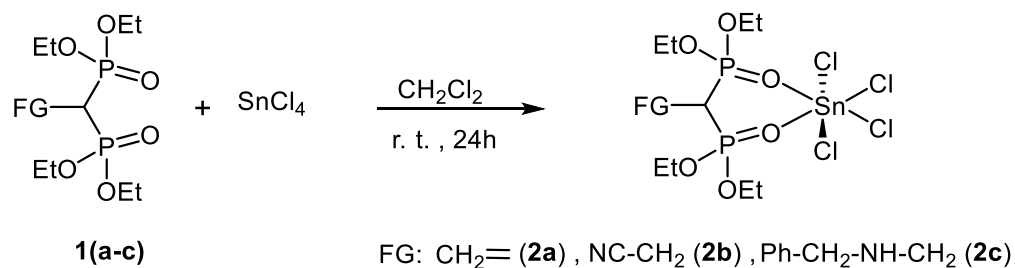
3.1. Synthesis

Tetraethyl ethenylidene-1,1-bisphosphonate (**1a**) was prepared according to the reported procedure [23]. The ligands tetraethyl 2-cyano-ethylidene-1,1-bisphosphonate (**1b**) and tetraethyl 2-benzylamino-ethylidene-1,1-bisphosphonate (**1c**) were synthesized from the reaction of **1a** with potassium cyanide in aqueous ethanol [24], or with benzylamine in anhydrous DCM [25], respectively as described previously (Scheme 1).



Scheme 1. Synthesis of ligands **1(a-c)**.

SnCl₄ was then reacted with ligands L (L = **1a-c**) in anhydrous dichloromethane to produce complexes **2a-c** as white solids with the composition [SnCl₄L]. Complex **2a** is soluble in chloroform and dichloromethane; **2c** is partially soluble in a mixture of CHCl₃-DMSO, while **2b** is poorly soluble in almost all common organic solvents. The complexes were characterized by elemental analysis, IR and in particular by their multinuclear NMR data and comparison with the corresponding data for the free ligands. The structure of **2b** has been determined by X-ray crystallography. The possible structures of complexes **2(a-c)** are shown in Scheme 2.



Scheme 2. Synthesis of complexes **2(a-c)**.

3.2. Spectroscopic characterization

The infrared spectra show strong bands within the range 1226-1255 cm^{-1} attributed to $\nu_{(\text{P}=\text{O})}$. The (P=O) stretching vibration is shifted towards lower wave numbers upon coordination to the tin atom, when compared with its value in the free ligands. The coordination shift is consistent with phosphoryl coordination to the tin atom. This shift is 83, 136 and 63 cm^{-1} for **2a**, **2b** and **2c**, respectively, explaining the relative difference in the basicity strength between the ligands **1a-c** (Table 2). The absorption band at 500-552 cm^{-1} corresponds to the stretching vibration of the Sn-O group, in good agreement with literature data for related complexes [15-19]. Interestingly, the CN stretching vibration in complex **2b** displaying medium absorption at 2246 cm^{-1} , remains approximately unchanged compared to the cyano group in the free ligand **1b** ($\nu_{\text{CN}} = 2226 \text{ cm}^{-1}$). Moreover, the stretching vibration of secondary amino group in complex **2c** ($\nu_{\text{N-H}} = 3047 \text{ cm}^{-1}$) was also almost unchanged compared to its value in the free ligand **1c** ($\nu_{\text{N-H}} = 2998 \text{ cm}^{-1}$). This confirms that nitrogen atoms in ligands **1b** and **1c** were not involved in chelation with the tin center which occurs only through the P=O groups of bisphosphonate moiety.

Table 2. IR data (ν/cm^{-1}) for the complexes **2(a-c)** and their free ligands (L).

Compound	$\nu_{(\text{P}=\text{O})}$ L	$\nu_{(\text{P}=\text{O})}$ ($\Delta\nu_{\text{PO}}$) Complex	$\nu_{(\text{Sn-O})}$
2a	1255	1172 (83)	552
2b	1252	1116 (136)	500
2c	1226	1163 (63)	530

The NMR spectra of complexes **2a-c** were recorded in CH_2Cl_2 solution and the data obtained for these complexes and their ligands are summarized in Table 3.

The room temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of complexes **2(a-c)** showed only one signal. The ^{31}P NMR resonances of the bound ligands are shifted to lower frequencies compared with those of the free ligand (Table 3). The difference in the ^{31}P chemical shift between free and bound ligands is more important than that observed in ^{13}C and ^1H NMR spectra. The ^{31}P NMR spectra at low temperature also show one signal, with the appearance of Sn satellites corresponding to the expected two-bond phosphorus-tin coupling. This suggests that there is only one isomer with no appreciable dissociation at the temperature range studied (298-198K).

The corresponding ^{119}Sn spectra for complex **2a** exhibited, at room temperature one signal in the region of hexacoordinated tin species [26], which becomes a well-resolved triplet feature at 268K (Fig.1). This triplet resonance is due to ^{119}Sn - ^{31}P two-bond coupling. Clearly one tin species is present for **2a**, in which the tin atom is coupled to both phosphorus atoms of the bisphosphonate moiety in a bidentate fashion, showing that the only isomer observed is, as expected, the *cis*-[SnCl_4L]. This is in agreement with the ^{31}P NMR spectra where one signal displaying Sn satellites with the corresponding coupling constants was

observed (Table 3). Furthermore, the triplet observed in the ^{119}Sn NMR spectrum of **2a** indicates that only the two P=O groups of the ligand are bound to the tin center excluding any possible coordination through the vinyl moiety.

It is also important to note that ^{119}Sn and ^{31}P NMR spectra of solutions of the **2a** reaction crude product in a solvent mixture ($\text{CH}_2\text{Cl}_2/\text{DMSO}$: 3/1) were investigated. The spectra showed a slight broadening of the MNR signals at room temperature, which could be due to minute dissociation of the complex as further shown in ^{31}P NMR spectra at low temperature (268 K) where very small additional signal corresponding to free ligand could be detected, This indicates the relative stability of these complexes in solution even in the presence of small amounts of the coordinating solvent DMSO. Unfortunately, the very poor solubility of **2c** and **2b** prevented their ^{119}Sn NMR spectra being recorded. However, the solid ^{119}Sn MAS NMR spectrum of **2c** was measured and displayed a broad signal in the expected tin hexacoordinate region (Table 3). This may suggest that complex **2c** has a similar structure to **2a**.

The above spectroscopic data show that no nitrogen atom, albeit in suitable position, in complexes **2b** and **2c** is involved in coordination to the tin center and only the P=O groups were coordinated. This specific affinity of P=O towards tin is in fair agreement with our recent work on monodentate phosphonates containing even harder hydroxy groups [18, 19]. Further evidence supporting the above NMR and IR data comes from the solid state structure of the poorly soluble solid complex, **2b**, as will be detailed below.

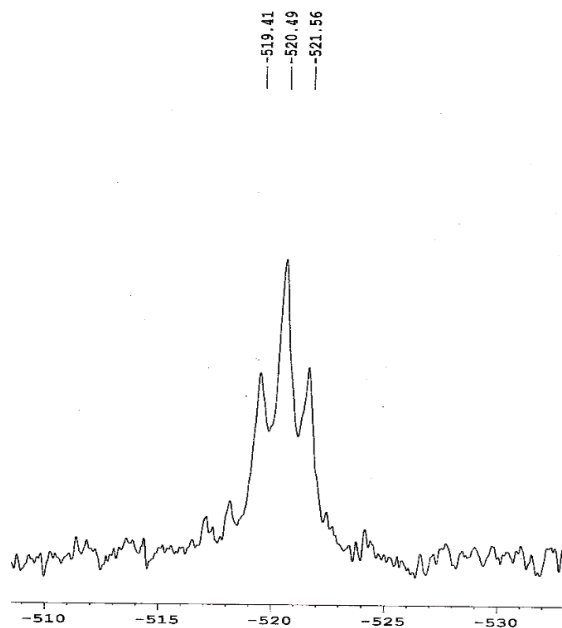


Fig. 1. ^{119}Sn NMR spectrum of **2a** in CH_2Cl_2 at 268 K.

Table 3. NMR data (δ /ppm and J/Hz) for complexes **2(a-c)** in CH₂Cl₂.

Compound	$\delta^{31}\text{P}$ ($^2J_{\text{P-Sn}}$) ^a	($\Delta\delta^{31}\text{P}$) ^b	$\delta^{119}\text{Sn}$ ($^2J_{\text{P-Sn}}$)
2a	10.7 (122)	2.1	-521 ^a (t, 121)
2b	18.6 (184)	2.7	-
2c	19.5 (189)	2.3	-520 ^c (bs)

^a Measured at 268 K (t: triplet).

^b $\Delta\delta^{31}\text{P} = (\delta^{31}\text{P})_{\text{L}} - (\delta^{31}\text{P})_{\text{complex}}$

^c Measured in solid state with ¹¹⁹Sn MAS NMR (bs: broad signal).

3.3. Single crystal X-ray diffraction analysis

The crystal structure of complex **2b** was elucidated after recrystallisation in DCM via slow evaporation at room temperature. The structure (Fig. 2, Table 4) reveals a distorted octahedral geometry at the tin composed of the chelating bisphosphonate (O–Sn–O = 98.46 and four chlorines with all the (*cis*) Cl–Sn–Cl angles 90° (range 92.59(6)–100.14(6)°). This is the first example of a tin bisphosphonate complex to be characterized via single crystal analysis. The Sn–Cl distances in the present complex (Sn–Cl_{transCl} = 2.817(2), 2.860(2) Å, Sn–Cl_{transO} = 2.792(2), 2.787(2) Å) may be compared with those reported in *trans*-[SnCl₄(HMPA)₂] [27] (2.863(3), 2.872(3) Å) and in *trans*-[SnCl₄((Me₂N)₂P(O)OCH₂CF₃)₂] [15] (Sn–Cl_{transCl} 2.781, 2.810, Sn–Cl_{transO} 2.780, 2.816 Å). The bond distances Sn–O = 2.120(5), 2.138(5) Å are similar to those in *trans*-[SnCl₄(HMPA)₂] 2.148, 2.119 Å [27].

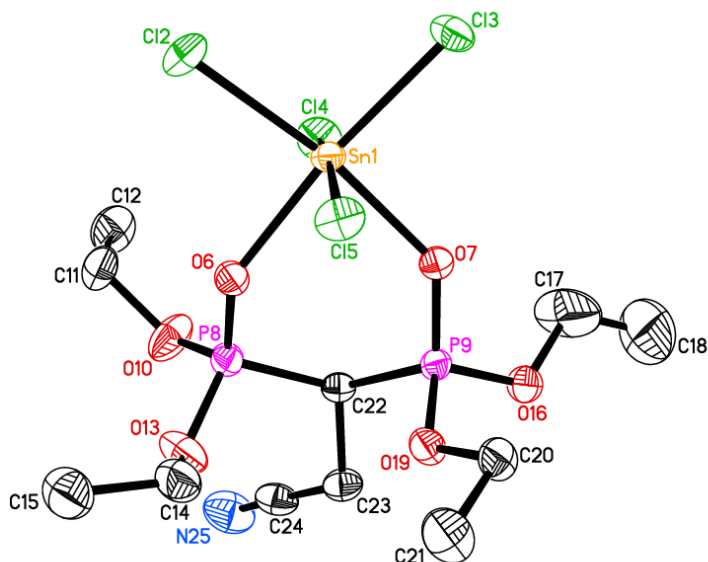


Fig. 2. The asymmetric unit of **2b**. Thermal ellipsoids are shown at 50% probability and all hydrogen atoms have been omitted for clarity.

Table 4. Selected bond lengths (Å) and angles (°) for the complex **2b**.

Bond length		Bond angle	
Sn(1)-O(6)	2.146(2)	Cl(5)-Sn(1)-O(6)	84.15(8)
Sn(1)-O(7)	2.134(3)	Cl(5)-Sn(1)-O(7)	85.08(8)
P(8)-O(6)	1.497(3)	O(6)-Sn(1)-O(7)	83.06(10)
P(8)-O(10)	1.546(3)	Sn(1)-O(7)-P(9)	135.95(16)
P(8)-O(13)	1.542(3)	Sn(1)-O(6)-P(8)	137.99(18)
P(9)-O(7)	1.495(3)	O(7)-P(9)-C(22)	112.14(15)
P(9)-O(16)	1.551(3)	O(6)-P(8)-C(22)	112.44(16)
P(9)-O(19)	1.543(3)	P(8)-C(22)-P(9)	111.09(18)
P(8)-C(22)	1.812(4)	Cl(4)-Sn(1)-Cl(5)	167.52(4)
P(9)-C(22)	1.801(4)	Cl(2)-Sn(1)-Cl(3)	98.51(4)

4. Conclusion

We have synthesized three new tin(IV) adducts with functionalized bisphosphonate ligands. The complexes were characterized by IR, multinuclear (^{31}P , ^{13}C and ^{119}Sn) NMR spectroscopy, and in the solid state for one case by single crystal X-ray diffraction. Despite the presence of the nitrogen atom in a suitable position in the title ligands, only the P=O groups were shown to be involved in coordination with the tin center producing chelate complexes **2(a-c)**. The reactivity of ligands **1(a-c)** towards other tin(IV) salts as well as other metal ions is now under investigation.

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