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Dibenzyltin(IV) complexes of the 5-[(*E*)-2-(aryl)-1-diazenyl]quinolin-8-olates: Synthesis and an investigation of structures by X-ray diffraction, solution and solid-state tin NMR, ^{119}Sn Mössbauer and electrospray ionization MS

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Abstract

A series of *cis*-bis{5-[(*E*)-2-(aryl)-1-diazenyl]quinolinolato}dibenzyltin(IV) complexes have been synthesized by reacting sodium salts of 5-[(*E*)-2-(aryl)-1-diazenyl]quinolin-8-ol (LH) and dibenzyltin dichloride. These complexes have been characterized by ^{1}H, ^{13}C, ^{119}Sn NMR, ESI-MS in solution and by IR and ^{119m}Sn Mössbauer, ^{117}Sn CP-MAS NMR spectroscopy in solid state. In addition, the structures of three of the dibenzyltin(IV) complexes, viz., $Bz_2Sn(L^2)_2$ (**2**), $Bz_2Sn(L^3)_2$ (**3**), and $Bz_2Sn(L^5)_2$ (**5**) (L = 5-[(*E*)-2-(aryl)-1-diazenyl]quinolin-8-ol: aryl = 4′-methylphenyl- (L^2H), 4′-methoxylphenyl- (L^3H) and 4′-bromophenyl- (L^5H)) were determined by single-crystal X-ray diffraction. In general, the complexes were found to adopt a distorted *cis*-octahedral arrangement around the tin atom in both solution and solid state.

Keywords: 5-[(*E*)-2-(aryl)-1-diazenyl]quinolin-8-ol; Dibenzyltin(IV) complexes; Solution and solid-state tin NMR; ESI-MS; ^{119m}Sn Mössbauer; Crystal structures

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1. Introduction

Recently, we have elucidated the X-ray structures of $Ph_2Sn(Ox)_2$ (Ox = deprotonated quinolin-8-ol) [1] and three *cis*-bis{5-[(*E*)-2-(aryl)-1-diazenyl]quinolinolato}diphenyltin(IV), $Ph_2Sn(L)_2$ (aryl = phenyl, 4′-methylphenyl and 4′-bromophenyl) complexes [2]. The X-ray results for the complexes indicated a distorted *cis*-octahedral geometry where the phenyl ligands are *cis* to one another and *trans* to the nitrogen atoms of the oxinate ligands. The complexes retain their solid-state structures, in solution, as revealed by the ^{119}Sn NMR spectroscopic results. Based on the multinuclear NMR (^{1}H, ^{13}C, ^{15}N and ^{119}Sn) chemical shifts and coupling constants, e.g., $^{n}J(^{119}\text{Sn}, ^{13}\text{C})$ (n = 1–5), $J(^{119}$Sn,

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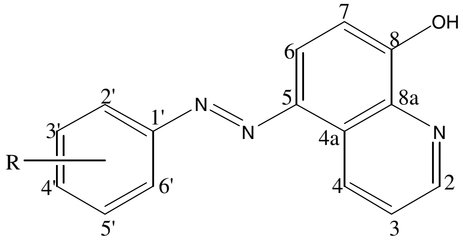

Fig. 1. Generic structure of the ligand (*Abbreviations.* L^1H, R = 3′-CH_3; L^2H, R = 4′-CH_3; L^3H, R = 4′-OCH_3; L^4H, R = 4′-OC_2H_5; L^5H, R = 4′-Br; L^6H, R = 4′-Cl, where H represents hydroxyl proton).

^{15}N) and ($^2J(^{15}N, ^1H)$), Holeček et al. have shown that in solutions of non-coordinating solvents, the organotin(IV) oxinates and thiooxinates exist as molecular chelates with a medium-to-strong Sn–N donor–acceptor bond [3–7]. The strength of the Sn–N bond depends on the nature and the number of organic substituents (bond strength generally increases with a decrease in the number of substituents and in the series phenyl ~vinyl > benzyl > *n*-butyl) as well as on the ligand composition [5–7]. Although, NMR spectroscopy is an important tool for investigating molecular structure in solution, however, the interpretation of chemical shifts and coupling constants, is generally based on X-ray crystal structure data and is consequently subject to uncertainties ranging from solvation to dynamic effects. Recently, we showed [8] that the solid-state tin NMR measurements on crystalline compounds can be used to deduce their structures. In view of this, a systematic approach was employed to determine the structures of several dibenzyltin(IV) complexes of 5-[(*E*)-2-(aryl)-1-diazenyl]quinolin-8-ol ligand system (Fig. 1) using ^1H, ^{13}C, ^{119}Sn NMR, ESI-MS, IR and ^{119m}Sn Mössbauer spectroscopic techniques in combination with solid-state ^{117}Sn NMR and X-ray diffraction.

2. Experimental

2.1. Materials

Bz_2SnCl_2 (dibenzyltin dichloride) was prepared by the method reported earlier [9]. The solvents used were of AR grade and dried using standard procedures. Benzene was distilled from sodium benzophenone ketyl.

2.2. Physical measurements

Carbon, hydrogen and nitrogen analyses were performed using a Perkin–Elmer 2400 series II instrument. IR spectra in the range 4000–400 cm^{-1} were obtained on a BOMEM DA-8 FT-IR spectrophotometer as KBr discs. The two-dimensional NMR experiments (see Section 3.4) for the ligands were performed on a Bruker Avance 500 spectrometer equipped with a triple ($^1H/^{13}C$/broad band) 5 mm inverse probe operating at 500.13 and 125.76 MHz, respectively. For the organotin compounds, the ^1H, ^{13}C and ^{119}Sn NMR spectra were recorded on a Bruker AMX 400 spectrometer and measured at 400.13, 100.62 and 149.18 MHz, respectively. The ^1H, ^{13}C and ^{119}Sn chemical shifts were referenced to Me_4Si set at 0.00 ppm, $CDCl_3$ set at 77.0 ppm and Me_4Sn set at 0.00 ppm, respectively. CP-MAS ^{117}Sn spectra were recorded at 89.15 MHz on a Bruker Avance 250 spectrometer, equipped with a 4 or 7 mm MAS broadband probe. ^{117}Sn was chosen instead of the more common ^{119}Sn nucleus, since the latter is interfering with RF radiation from a local radio station. Spinning frequencies are chosen between 5 and 8 kHz. A contact time of 1 ms and a recycle delay of 2 s were employed. The chemical shift reference was set using (cyclo-$C_6H_{11})_4Sn$ (−97.35 ppm relative to $(CH_3)_4Sn$). The principle values of the ^{117}Sn chemical shielding tensors were determined by fitting the intensities of the spinning side bands according to the Herzfeld–Berger formalism, using the ‘dmfit’ program (Massiot D. *dmfit program*; available at http://crmht-europe.cnrs-orleans.fr). Positive-ion and negative-ion electrospray ionization (ESI) mass spectra were measured on an ion trap analyzer Esquire 3000 (Bruker Daltonics, Bremen, Germany) in the range *m*/*z* 50–1500. The samples were dissolved in acetonitrile and analyzed by direct infusion using a flow rate 5 μl/min. The selected precursor ions were further analyzed by MS/MS analyses under the following conditions: the isolation width *m*/*z* = 8, the collision amplitude in the range 0.7–1.0 V depending on the precursor ion stability, the ion source temperature 300 °C, the tuning parameter compound stability 100%, the flow rate and the pressure of nitrogen 4 l/min and 10 psi, respectively [10,11]. The Mössbauer spectra of the complexes in the solid state were recorded using a Model MS-900 (Ranger Scientific Co., Burleson, TX) spectrometer in the acceleration mode with a moving source geometry. A 10 mCi $Ca^{119m}SnO_3$ source was used, and counts of 30,000 or more were accumulated for each spectrum. The spectra were measured at 80 K using a liquid-nitrogen cryostat (CRYO Industries of America, Inc., Salem, NH). The velocity was calibrated at ambient temperature using a composition of $BaSnO_3$ and tin foil (splitting 2.52 mm s^{-1}). The resultant spectra were analyzed using the Web Research software package (Web Research Co., Minneapolis, MN).

2.3. Synthesis of 5-[(E)-2-(aryl)-1-diazenyl]quinolin-8-ols

The 5-[(*E*)-2-(aryl)-1-diazenyl]quinolin-8-ols, viz., L^1H, L^2H, L^4H, L^5H were prepared by the method described earlier [2]. However, the other quinolinols, viz., L^3H, L^6H, were prepared analogously with the appropriate anilines and their analytical and spectroscopic data are presented below.

2.3.1. Preparation of 5-[(E)-2-(4-methoxyphenyl)-1-diazenyl]quinolin-8-ol (L^3H)

Recrystallized from methanol to give a brownish yellow precipitate in 44.1% yield; m.p. 170–171 °C. Anal. Calc. for