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Research paper

Supramolecular architecture of organotin(IV) *N*-methyl ferrocenyl *N*-ethanol dithiocarbamates: Crystallographic and computational studies

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ABSTRACT

Four new organotin(IV) ferrocenyl dithiocarbamate complexes *viz.* $[(FcCH_2EtOHdtc)_2SnR_2]$ (R = Me (**1**), *n*-Bu (**2**) and Ph (**3**)) and $[(FcCH_2EtOHdtc)SnPh_3]$ (**4**) have been synthesized and characterized by electronic absorption, IR, ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopy. The molecular structures of **1** and **2** have been confirmed by single crystal X-ray diffraction technique. The X-ray analyses for **1** and **2** reveal a skew trapezoidal bipyramid geometry around Sn(IV) which is being satisfied by the two sulfur atoms of the two dithiocarbamate ligands in anisobidentate fashion. In the crystal structure of **1**, an interesting one dimensional chain held by O—H···O intermolecular interactions and also display weak C—H···π and C—H···S interactions. The crystal structure of **2** exhibit the formation of one dimensional chain held by weak O—H···S, (Cp)C—H···O and π···π interactions. Additionally **2** also display the formation of one dimensional chain because of the (Cp)C—H···S and (Cp)C—H···π interactions. These interactions have been addressed by ab initio and atoms-in-molecules analyses.

1. Introduction

In the recent years, amongst dithiolates, the dithiocarbamates have received substantial extent of consideration as prospective ligand systems for main group, transition metal and organometallic building blocks [1–5]. This is because of its easy methodology of syntheses, strong coordination ability and its capability to produce coordination-driven self-assembly. Also, this class finds utility in a variety of research areas *viz.* materials science and supramolecular chemistry and has shown imperative biological activities [1–5]. During the last few years the dithiocarbamate chemistry is concentrated upon the functionalization of the ancillary region of the dithiocarbamate which can develop fascinating supramolecules through non-covalent interactions *viz.* O···H, N···H, π···π and C—H···π (chelate, CS_2M) in solid state [1–8]. These different interactions are capable of giving rise to physical properties which can be tuned by changing the nature of the substituents [1–8].

The inherent Lewis acidity of organotin(IV) halides makes them an ideal candidate for synthesizing complexes with dithiocarbamates and the resulting products shows substantial tendency to generate self-assembled supramolecular architecture [9] and can also offer a platform for the formation of macrocycles [3h,i]. Additionally, organotin(IV) dithiocarbamates have shown application in the area of medicinal chemistry because of the unique stereo-electronic properties of organotin(IV) centers bonded to the sulfur of dithiocarbamate ligands [10]. Also, they find applications in the field of material chemistry as the single source precursors for tin sulfide which is IV–VI semiconductor [11]. Molecular recognition studies with organotin(IV) dithiocarbamates indicated that they can function as receptors for neutral and anionic substrates particularly for the carboxylate anionic derivatives [12]. The interest in organometallic chemists for this class of organometallic system have been develop because of the capability of organotin(IV) derivatives to form complexes with dtc ligands through self-assembly and, hence offering the possibility to form macrocyclic assemblies in one-pot synthetic procedures [13]. Although organotin(IV) compounds of the type comprising of aromatic or aliphatic substituents at the

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dithiocarbamate fragment are abundant [1–13] but those featuring a ferrocenyl pendant on the dithiocarbamate entity are scarce [14]. We expect that exploration of the synthetic routes and as well as investigation of new types of secondary interactions *viz.* intermolecular O···H, (Cp)C—H···O and π···π interactions in organotin(IV) dithiocarbamates bearing ferrocenyl pendants would be interesting. With these views, we herein report the synthesis, characterization and molecular and supramolecular structures of new organotin(IV) dithiocarbamates comprising of ferrocenyl pendant and also having an —OH group at the periphery of the ligand. The nature of interaction in supramolecular motifs and their energies have been addressed using MP2 calculations and further these interactions have been validated using the Atoms in Molecules (AIM) theory.

2. Experimental

2.1. Materials and methods

All chemical reagents are commercially available and were used without further purification. Infrared spectra were recorded as KBr pellets on a Shimadzu IR Affinity IS FTIR spectrophotometer. ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded on Bruker Avance IIIHD 300 MHz spectrophotometers. Chemical shifts were reported in parts per million using TMS as internal standard for ^{1}H and ^{13}C NMR and tetramethyltin for ^{119}Sn NMR. The potassium salt of *N*-methylferrocenyl *N*-ethanol dithiocarbamate (KFcCH$_2$EtOHdtc) had been synthesized in accordance with our previously reported method [5g].

2.2. Syntheses

2.2.1. Synthesis of [(FcCH$_2$EtOHdtc)$_2$SnR$_2$] (R = Me (**1**), Bu (**2**) and Ph (**3**))

The dithiocarbamate KFcCH$_2$EtOHdtc (0.373 g, 1 mmol) was dissolved into the methanol and to this dimethyl tin(IV)dichloride (0.110 g, 0.5 mmol)/di-*n*-butyl tin(IV)dichloride (0.152 g, 0.5 mmol)/diphenyl tin(IV) dichloride (0.172 g, 0.5 mmol) dissolved in dichloromethane was added dropwise under nitrogen atmosphere. The reaction mixtures were stirred for 2 h and then evaporated up to dryness. The dried product was dissolved in dichloromethane and filtered through Celite, concentrated and finally precipitated with petroleum ether.

2.2.1.1. Characterization data. **1**: yield (0.680 g, 83.02%); m. p. 125 °C; IR (KBr): ν = 3376 (O—H), 1468 (C=N), 1077 (C—S), cm^{-1}; ^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 4.86 (s, 4H, Fc—CH$_2$), 4.33 (s, 4H, Fc—H), 4.16 (s, 14H, Fc), 3.89 (d, *J* = 4.5, 4H, CH$_2$CH$_2$OH), 3.83 (d, *J* = 4.2, 4H, CH$_2$CH$_2$OH), 1.18 (s, 6H, CH$_3$) ppm; ^{13}C NMR (75.50 MHz, CDCl$_3$): δ = 200.8 (CS$_2$), 81.6 (FcCC), 70.1 (FcCH), 68.8 (FcCH), 60.6 (FcCH$_2$), 55.1 (CH$_2$CH$_2$OH), 54.7 (CH$_2$CH$_2$OH), 29.8 (CH$_3$); ^{119}Sn NMR (111.90 MHz, CDCl$_3$): δ = −331.2.

2: yield (0.540 g, 59.80%); m. p. 174 °C; IR (KBr): ν = 3399 (O—H), 1466 (C=N), 1049 (C—S), cm^{-1}; ^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 4.96 (s, 4H, Fc—CH$_2$), 4.41 (s, 4H, Fc—H), 4.18 (s, 14H, Fc), 3.99 (t, *J* = 5.1, 4H, CH$_2$CH$_2$OH), 3.91 (t, *J* = 4.8, 4H, CH$_2$CH$_2$OH), 2.11 (t, *J* = 6.9, 4H, CH$_2$), 1.95 (m, 4H, CH$_2$), 1.51 (m, 4H, CH$_2$), 0.94 (t, *J* = 7.2, 6H, CH$_3$) ppm; ^{13}C NMR (75.50 MHz, CDCl$_3$): δ = 200.1 (CS$_2$), 81.8 (FcCC), 70.1 (FcCH), 68.7 (FcCH), 60.8 (FcCH$_2$), 54.9 (CH$_2$CH$_2$OH), 54.6 (CH$_2$CH$_2$OH), 34.8 (CH$_2$), 28.7 (CH$_2$), 26.6 (CH$_2$), 14.1 (CH$_3$); ^{119}Sn NMR (111.90 MHz, CDCl$_3$): δ = −334.6.

3: yield (0.592 g, 62.74%), m. p. 90 °C; IR (KBr): ν = 3403 (O—H), 1487 (C=N), 1081 (C—S) cm^{-1}; ^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 7.99 (d, *J* = 6.0, 4H, C$_6$H$_5$), 7.83 (d, *J* = 6.6, 4H, C$_6$H$_5$), 7.41 (m, 2H, C$_6$H$_5$) 4.80 (s, 4H, Fc-CH$_2$), 4.32 (s, 4H, Fc—H), 4.13 (s, 4H, Fc—H), 4.09 (S, 10H, Fc—H), 3.79 (S, 8H, CH$_2$CH$_2$OH), ppm; ^{13}C NMR (75.45 MHz, CDCl$_3$): δ = 200.2 (CS$_2$), 150, 135.9, 134.4, 128.4 (C$_6$H$_5$), 81.4 (FcCC), 70.1 (FcCH), 69.6 (FcCH), 65.6 (FcCH), 60.3 (FcCH$_2$), 55.6 (CH$_2$CH$_2$OH), 48.1 (CH$_2$CH$_2$OH); ^{119}Sn NMR (111.90 MHz, CDCl$_3$): δ = −491.6.

2.2.2. Synthesis of [(FcCH$_2$EtOHdtc)SnPh$_3$] (**4**)

The dithiocarbamate KFcCH$_2$EtOHdtc (0.373 g, 1 mmol) was dissolved in methanol and to this triphenyl tin(IV)chloride (0.385 g, 1 mmol) dissolved in dichloromethane was added dropwise under nitrogen atmosphere. The reaction mixture was stirred for 2 h and the evaporated to dryness. The dried product was dissolved in dichloromethane and filtered through Celite, concentrated and finally precipitated with petroleum ether.

4: yield (0.392 g, 57.20%), m.p.110 °C; IR (KBr): ν = 3425 (O—H), 1496 (C=N), 1063 (C—S) cm^{-1}; ^{1}H NMR (300.13 MHz, CDCl3): δ = 8.06 (d, *J* = 5.7, 6H, C$_6$H$_5$), 7.91 (d, *J* = 6.3, 6H, C$_6$H$_5$), 7.47 (m, 3H, C$_6$H$_5$), 4.93 (s, 2H, Fc—CH$_2$), 4.40 (s, 2H, Fc—H), 4.20 (s, 2H, Fc), 4.16 (s, 5H, Fc), 3.85 (t, *J* = 16.5, 8H, CH$_2$CH$_2$OH), ppm; ^{13}C NMR (75.45 MHz, CDCl$_3$): δ = 200.8 (CS$_2$), 142.1, 135.9, 134.4, 129.1 (C$_6$H$_5$), 81.4 (FcCC), 70.1 (FcCH), 68.8 (FcCH), 64.8 (FcCH) 60.4 (FcCH$_2$), 56.5 (CH$_2$CH$_2$OH), 55.7 (CH$_2$CH$_2$OH); ^{119}Sn NMR (111.90 MHz, CDCl$_3$): δ = −491.2, −321.3.

2.3. X-ray crystallography

Intensity data for **1** and **2** were collected at 150(2) K on a Rigaku Xcalibur, EosS2 single crystal diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Unit cell determination, data collection and data reduction were performed using the CrysAlisPro software [15]. A symmetry-related (multi-scan) absorption correction had been applied. The structures were solved with SHELXT [16] and refined by a full-matrix least-squares procedure based on F^2 (Shelxl-2014) [17]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed onto calculated positions and refined using a riding model except for the OH hydrogen atoms which have been located in the difference Fourier map and were refined with bond lengths restraints. In **1** both EtOH groups are disordered over two sites in the ratio 1:1 as they are connected to each other through intermolecular hydrogen bonding. However, the OH hydrogen atoms could only be refined using geometric constraints. Atoms C13 and C13A had to be refined with ADP restraints because of their proximity to each other. Additional programs used for analysing data and their graphical manipulation included: SHELXle [18] and ORTEP 3 for windows [19]. The pertinent crystallographic data and refinement parameters for **1** and **2** are presented in Table 1.

2.4. Computational details

Molecular geometries were optimized at the level of density functional theory (DFT) using the B3LYP functional [20]. The split valence basis sets, 6-31G** were used for all C, N, O, S, and H atom centers. LANL2DZ basis set was used for the Sn and Fe atom centers. The intermolecular interaction energies have been estimated at the MP2 level of theory [21]. For the interaction energy calculations, the interaction distances have been fixed for the dimer or trimer while all other degrees of freedom were relaxed in the geometry optimization. The stabilization energies (ΔE_{dimer} and ΔE_{trimer}) for dimeric and trimeric motifs involving the 2 and 3 molecules, respectively were calculated using the formula $\Delta E_{\text{dimer}} = E_{\text{dimer}} - (2 \times E_{\text{monomer}})$ and $\Delta E_{\text{trimer}} = E_{\text{trimer}} - (3 \times E_{\text{monomer}})$ where E_{monomer}, E_{dimer}, E_{trimer} are the energies of the monomer, dimer