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Di- and tri-organotin(IV) complexes of the new bis(1-methyl-1*H*-imidazol-2-ylthio)acetate ligand and the decarboxylated analogues

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Abstract

The new sodium bis(1-methyl-1*H*-imidazol-2-ylthio)acetate, Na[(*S*-tim)$_2$CHCO$_2$], has been prepared in ethanol solution using 2-mercapto-1-methylimidazole, dibromoacetic acid and NaOH. New di- and tri-organotin(IV) derivatives have been synthesized from reaction between SnR_nCl_{4-n} (R = Ph, Cy and ^{n}Bu, $n = 2$–3) acceptors and Na[(*S*-tim)$_2$CHCO$_2$]. Complexes of the type {[κ^1*O*-(*S*-tim)$_2$CHCO$_2$]SnR$_3$} and related decarboxylated species {[κ^2*N*,*N*-(*S*-tim)$_2$CH$_2$]SnR$_2$Cl$_2$} have been obtained and characterized by elemental analyses, FT-IR, ESIMS and multinuclear (^{1}H, ^{13}C and ^{119}Sn) NMR spectral data. The adduct {κ^1*O*-[(*S*-tim)$_2$CHCO$_2$]Sn(H$_2$O)(C$_4$H$_9$)$_3$} was characterized by single crystal X-ray studies. The dichloromethane reaction solution of {κ^1*O*-[(*S*-tim)$_2$CHCO$_2$]Sn(C$_6$H$_5$)$_3$} was re-crystallized and the decarboxylated species {[(*S*-tim)$_2$CH$_2$]SnCl(H$_2$O)(C$_6$H$_5$)$_3$} was obtained as a crystalline solid and characterized by X-ray crystallography.

Keywords: Organotin(IV); Scorpionates; Methimazole; X-ray; Spectroscopy

1. Introduction

Organotin compounds occupy an important place in academic research, as well as in industrial chemistry; they are of interest in view of the considerable structural diversity that they possess. This aspect has been attracting the attention of a number of researchers and a multitude of structural types have been discovered [1–3]. Many organotin compounds have been tested for their *in vitro* activity against a large variety of tumor lines [4–6]. Recently organotin compounds have been used as reagents in reduction, transmetallation and coupling reactions or as extremely versatile catalysts in organic reactions [7–14]; the generally high selectivity of organotin reagents allows one to save time and to avoid product losses of protection–deprotection cycles. In industry, organotin compounds are utilized for esterification and transesterification reactions, for silicone curing, for the preparation of polyurethanes [15], but the stabilization of poly(vinyl chloride) (PVC) is their largest application so far [16]. Organotin have been known for their excellent biocidal properties and they are used in agricultural biocides and additives for antifouling paints for marine transport vessels [17]. In the investigation of the possible utility of triorganotin trichloroacetates as CX$_2$ transfer agents it was found that they decompose with carbon dioxide evolution in the presence of an olefin [18].

Recently, we have reported the synthesis and the spectroscopic characterization of new poly(pyrazolyl)borate

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[19,20] and poly(imidazolyl)borate [21,22] complexes containing organotin(IV) acceptors. It has been our endeavor to develop the chemistry of organotin compounds bearing co-ligands of ambidentate character. The primary impetus has been to comprehend competitive coordination modes of poly(azolyl)borate ligands to the tin atom and find a rationale related to the stability and structural motifs of this class of compounds [23]. As an extension of this research field, we have developed the chemistry of some new organotin carboxylates obtained by the interaction of a number of organotin(IV) halides with new polyfunctional S,N,O-ligands, containing two pyridine groups and other biologically relevant hydrophilic moieties, such as carboxylate groups [24].

In recent years, a number of authors [25–34] have synthesized S,N-ligands of the type $(CH_2)_n(SAz)_2$ based on a nitrogenated aromatic ring system such as benzimidazole or pyridine. These ligands are able to coordinate by both S and the neighbouring N atom, and hence to form stable chelate rings of five or more atoms [35–41]. In particular, Gardinier [42,43] and Casas [44] have recently reported the synthesis, the analytic, spectroscopic and structural characterization of the bis(thioimidazolyl)methane family of compounds. These compounds are attractive owing to both their potential biomedical applications [45,46] and their potential utility in fundamental coordination chemistry [44,47–51].

Bearing in mind the above, we have developed a strategy for producing a new class of monoanionic and polyfunctional N,O,S-ligands of possible considerable coordinative flexibility. Towards this end, we report now the synthesis and characterization of the new sodium bis(1-methyl-1*H*-imidazol-2-ylthio)acetate ligand, Na[(*S*-tim)$_2$CHCO$_2$] (Fig. 1) and its interaction with a number of di- and triorganotin(IV) halides. Complexes of the type {[κ^1*O*-(*S*-tim)$_2$CHCO$_2$]SnR$_3$} and related decarboxylated species {[κ^2*N*,*N*-(*S*-tim)$_2$CH$_2$]SnR$_2$Cl$_2$} have been obtained and characterized. Since carboxylic acid derivatives are ubiquitous synthetic building blocks, the ability to access reactive organometallic species via decarboxylation offers clear practical advantages [52–56].

2. Materials and methods

2.1. General procedures

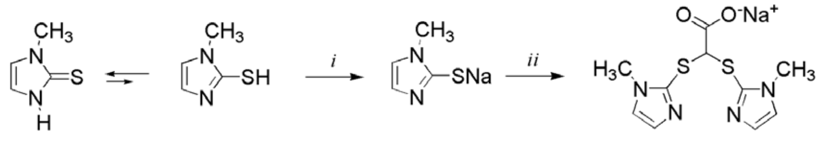
All syntheses and handling were carried out under an atmosphere of dry oxygen-free dinitrogen, using standard Schlenk techniques or a glove box. All solvents were dried, degassed and distilled prior to use. Elemental analyses (C,H,N,S) were performed in house with a Fisons Instruments 1108 CHNS-O Elemental Analyser. Melting points were taken on an SMP3 Stuart Scientific Instrument. Thermal Analysis was performed using a power compensation Differential Scanning Calorimeter (DSC Pyris1, Perkin–Elmer US Instrument Division, Norwalk, CT 06859 USA); the instrument was previously calibrated for melting enthalpy and temperature using high grade purity Indium as a standard. IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin–Elmer System 2000 FT-IR instrument. IR annotations used: br = broad, m = medium, mbr = medium broad, s = strong, sbr = strong broad, sh = shoulder, w = weak. ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded on a Oxford-400 Varian spectrometer (400.4 MHz for ^{1}H, 100.1 MHz for ^{13}C and 149.3 MHz for ^{119}Sn). NMR annotations used: m = multiplet, s = singlet. Electrospray mass spectra (ESIMS) were obtained in positive- or negative-ion mode on a Series 1100 MSD detector HP spectrometer, using an acetone mobile phase. The compounds were added to the reagent grade methanol to give solutions of approximate concentration 0.1 mM. These solutions were injected (1 μL) into the spectrometer via a HPLC HP 1090 Series II fitted with an autosampler. The pump delivered the solutions to the mass spectrometer source at a flow rate of 300 μL min^{-1}, and nitrogen was employed both as a drying and nebulizing gas. Capillary voltages were typically 4000 V and 3500 V for the positive- and negative-ion mode, respectively. Confirmation of all major species in this ESIMS study was aided by comparison of the observed and predicted isotope distribution patterns, the latter calculated using the ISOPRO 3.0 computer program.

3. Experimental

3.1. Synthesis

3.1.1. Na[(*S*-tim)$_2$CHCO$_2$] (**1**)

2-Mercapto-1-methylimidazole (5.000 g, 43.8 mmol) was added to a solution of NaOH (4.380 g, 109.5 mmol) in 100 mL of absolute ethanol. After 12 h stirring, a solution of dibromoacetic acid (4.770 g, 21.9 mmol) in 40 mL of absolute ethanol was added dropwise to the sodium salt so obtained, and this mixture was stirred at gentle reflux for 6 h to give an orange emulsion. The mixture was allowed to cool to rt, filtered and then concentrated



Na[(S-tim)$_2$CHCO$_2$], **1**

Fig. 1. Synthesis of the sodium bis(1-methyl-1*H*-imidazol-2-ylthio)acetate ligand, Na[(*S*-tim)$_2$CHCO$_2$], starting from 2-mercapto-1-methylimidazole. Conditions: (i) NaOH in ethanol solution, r.t., 12 h; (ii) dibromoacetic acid, reflux, 6 h.