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Synthesis and characterization of new organotin(IV) complexes with polyfunctional ligands

Maura Pellei [a,*], Giancarlo Gioia Lobbia [a], Marilena Mancini [a],
Riccardo Spagna [b], Carlo Santini [a]

[a] Dipartimento di Scienze Chimiche, Università di Camerino, via S. Agostino 1, 62032 Camerino, Macerata, Italy
[b] Istituto di Cristallografia, CNR, Sezione di Monterotondo, C.P. No. 10, 00016 Monterotondo Stazione, Roma, Italy

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Abstract

New mono-, di- and tri-organotin(IV) derivatives containing the neutral bis(2-pyridylthio)methane ligand, [$(pyS)_2CH_2$] and tris(2-pyridylthio)methane ligand, [$(pyS)_3CH$] have been synthesized from reaction with SnR_nCl_{4-n} (R = Me, ^{n}Bu, Ph and Cy, $n = 1$–3) acceptors. Mono-nuclear adducts of the type {[$(pyS)_2CH_2$]R_nSnCl_{4-n}} and {[$(pyS)_3CH$]R_nSnCl_{4-n}} have been obtained and characterized by elemental analyses, FT-IR, ESI-MS, multinuclear (^1H and ^{119}Sn) NMR spectral data. The ^1H and ^{119}Sn NMR and ESI-MS data suggest for the triorganotin(IV) derivatives a complete dissociation of the compounds in solution. The mono- and di-organotin(IV) derivatives show a greater stability in solution, and their spectroscopic data are in accordance with the existence of six-coordinated $RSnCl_3N_2$ or $R_2SnCl_2N_2$ species.

Keywords: Organotin(IV); Bis(2-pyridylthio)methane; Tris(2-pyridylthio)methane; 2-Mercaptopyridine; Tin-119 NMR; Electrospray ionization mass spectroscopy

1. Introduction

The interest in the coordination chemistry of tin and organotin acceptors with poly(azolyl)alkanes, β-diketones and poly(azolyl)borates dates from a long time. Organotin(IV) compounds are of interest in view of the considerable structural diversity that they possess and an additional reason for this research field is based on the biological activity, antifouling paints and antitumor activity displayed by many organotin(IV) derivatives containing mixed N,X-ligands (X = O, S, P) [1,2].

Recently, we have reported the synthesis and the spectroscopic characterization of new poly(pyrazolyl)borate [3,4] and poly(imidazolyl)borate [5,6] 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 scorpionate ligands to the tin atom and find a rationale related to the stability and structural motifs of this class of compounds [7]. As an extension of this research field, we are now interested in the development of the chemistry of some new organotin compounds obtained from the interaction of a number of organotin(IV) halides with polyfunctional S,N-ligands, containing two or three pyridine groups.

In recent years a number of authors [8–17] have synthesized S,N-ligands of the type $(CH_2)_n(SAz)_2$ (Fig. 1) based on a nitrogenated aromatic ring system such as pyridine (Fig. 1(a)). These ligands are able to coordination by both S and the neighbouring N atom, and hence the formation of stable chelate rings of five or more atoms [18–25]. In particular the bis(2-pyridylthio)methane (Fig. 1(b)) has a rich coordination chemistry as recently reported for Zn(II), Hg(II), Cu(I), Ag(I) [26], Cd(II) [27] and Cu(II) [28]

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[*] Corresponding author. Tel.: +39 0737 402293; fax: +39 0737 637345.
E-mail address: maura.pellei@unicam.it (M. Pellei).

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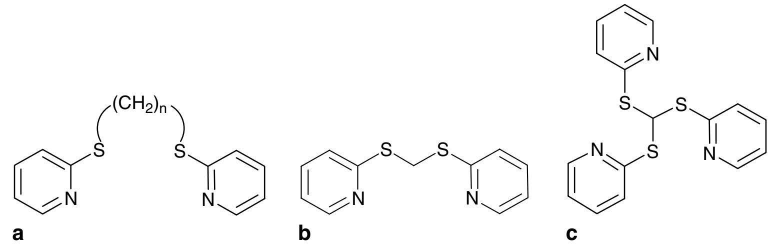

Fig. 1. Structure of S,N-ligands of type $(CH_2)_n(SAz)_2$.

complexes. Tris(2-pyridylthio)methane (Fig. 1(c)) has also been synthesized by Kinoshita et al. [28,29] and they have shown that this ligand reacts with copper(II) halide forming the first example of compounds containing a Cu(II)–C(sp^3) bond [30].

Recently, we have reported the synthesis, characterization and hydrolytic behavior of some new complexes obtained from the interaction of a number of organotin(IV) halides with the novel sodium bis(2-pyridylthio)acetate ligand [31]. The spectroscopic and structural data suggest for these derivatives a strong bonding of the tin atom to the carboxylate group of the ligand.

We have extended this research to the coordination chemistry of two neutral pyridine-2-thiolate ligands, bis- and tris-(2-pyridylthio)methanes; they are particularly versatile sulphur-containing ligands suitable for the assembly of metallosupramolecular materials and of relevance in biological systems.

2. Experimental

2.1. Materials and methods

All reagents were purchased from Aldrich (Milwaukee) and used as received. All syntheses were carried out under a nitrogen atmosphere. All solvents were distilled and degassed with dry nitrogen prior to use. The samples for microanalysis were dried in vacuo to constant weight (20 °C, ca. 0.1 Torr). Elemental analyses (C, H, N, S) were performed with a Fisons Instruments 1108 CHNS-O Elemental analyser. IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin–Elmer System 2000 FT-IR instrument. ^1H and ^{119}Sn NMR spectra were recorded on a VXR-300 Varian instrument operating at room temperature (respectively, at 300 MHz for ^1H and 111.9 MHz for ^{119}Sn). Melting points were taken on an SMP3 Stuart Scientific Instrument. The electrical conductivity measurements (Λ_m, reported as $\Omega^{-1}\,cm^2\,mol^{-1}$) of acetone or dichloromethane solutions were taken with a Crison CDTM 522 conductimeter at room temperature. Electrospray mass spectra (ESI-MS) 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 $\mu l\,min^{-1}$, and nitrogen was employed both as a drying and nebulizing gas. Capillary voltages were typically 4000 and 3500 V for the positive- and negative-ion mode, respectively. Confirmation of all major species in this ESI-MS study was aided by comparison of the observed and predicted isotope distribution patterns, the latter calculated using the ISOPRO computer program [32].

2.2. Synthesis

2.2.1. Synthesis of $[(pyS)_2CH_2]$ (1)

The bis(2-pyridylthio)methane ligand was prepared by modification of the literature method [29]. The crude product was recrystallized in acetone/dichloromethane (1:1) yielding $[(pyS)_2CH_2]$ (**1**) as pale yellow microcrystalline needles. Yield: 88%. M.p. 92–95 °C. ^1H NMR ($CDCl_3$, 293 K): δ 5.07 (s, 2H, CH_2), 7.02 (m, 2H, 5-C*H*), 7.19 (d, 2H, 3-C*H*), 7.48 (m, 2H, 4-C*H*), 8.51 (d, 2H, 6-C*H*). IR (nujol, cm^{-1}): 3111w, 3070w, 3045w (CH), 1577s, 1557s (C=C + C=N), 665m, 620s, 477s, 444s, 419m, 397s, 378m, 356w, 257sbr. ESI-MS (major negative-ions, CH_3OH), m/z (%): 233 (100) $[(pyS)_2CH]^-$, 110 (50) $[(pyS)]^-$. Calc. for $C_{11}H_{10}N_2S_2$: C, 56.38; H, 4.30; N, 11.95; S, 27.36. Found: C, 56.23; H, 4.25; N, 11.83; S, 26.99%.

2.2.2. Synthesis of $[(pyS)_3CH]$ (2)

The tris(2-pyridylthio)methane ligand was prepared by modification of the literature method [29]. The crude product was recrystallized from diethyl ether. Yield: 66%. M.p. 106–109 °C. ^1H NMR ($CDCl_3$, 293 K): δ 7.02 (m, 3H, 5-C*H*), 7.25 (d, 3H, 3-C*H*), 7.52 (m, 3H, 4-C*H*), 7.91 (s, 1H, C*H*), 8.52 (d, 3H, 6-C*H*). IR (nujol, cm^{-1}): 3144w, 3107w, 3048w (CH), 1572s, 1555s (C=C + C=N), 616s, 481s, 452s, 395s, 344s, 322s, 279w, 264w, 235s, 224w, 206w. ESI-MS (major positive-ions, CH_3OH), m/z (%): 344 (100) $[\{(pyS)_3CH\} + H]^+$, 366 (30) $[\{(pyS)_3CH\} + Na]^+$, 710 (60) $[2\{(pyS)_3CH\} + Na]^+$. ESI-MS (major negative-ions, CH_3OH), m/z (%): 379 (100) $[(pyS)_3CH + Cl]^-$, 342 (20) $[(pyS)_3C]^-$, 110 (10) $[(pyS)]^-$. Calc. for $C_{16}H_{13}N_3S_3$: C, 55.95; H, 3.81; N, 12.23; S, 28.00. Found: C, 55.90; H, 3.70; N, 12.00; S, 27.80%.