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Mononuclear homoleptic organotin(IV) dithiocarbamates: Syntheses, structures and antimicrobial activities

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ABSTRACT

Six mononuclear organotin(IV) complexes of two dithiocarbamato ligands, $[Ph_3SnL^1]$ (**1**), $[Bu_2Sn(L^1)_2]$ (**2**), $[Ph_2Sn(L^1)Cl]$ (**3**), $[Ph_2Sn(L^1)_2]$ (**4**), $[Ph_2Sn(L^2)_2]$ (**5**) and $[Ph_3Sn(L^2)]$ (**6**) where $\mathbf{L^1}$ = thiomorpholine-4-carbodithiolate and $\mathbf{L^2}$ = 2,6-dimethylmorpholine-4-carbodithiolate have been synthesized in good yields. Both ligands and complexes **1**–**6** were characterized by elemental analyses, FT-IR spectroscopy, UV-visible spectroscopy and ^{1}H, ^{13}C{^{1}H} ^{119}Sn{^{1}H} NMR spectroscopy. In addition, the solid-state structures of the complexes were established through single-crystal X-ray diffraction analyses. The X-ray analyses reveal that the Sn(IV) center is five-coordinated in **1**, **3** and **6**. In complexes **2**, **4** and **5**, Sn(IV) is six-coordinated and occupies the center of a distorted octahedron. Moreover, an asymmetric coordination mode of the dithiocarbamato ligands was observed in all complexes. The optical properties and thermal stabilities of all complexes were investigated. All complexes were evaluated for their *in vitro* antimicrobial properties against *E. coli*. Complex **1** shows a maximal biological activity whereas the least activity is found for complex **6**.

1. Introduction

Organotin compounds have consistently been a potential area of research because of their immense structural diversities [1]. When combined with carboxylate ligands, organotin compounds exhibit a variety of structures ranging from monomers, dimers, oligomers, polymers and even, one-, two- or three-dimensional frameworks [2,3]. However, recent research work has been slowly replacing carboxylate ligands by sulfur donor ligands because of their resemblance with sulfur-containing biomolecules such as vitamins and amino acids [4]. In this context, the synthesis of metal complexes using a dithiocarbamate anion ($R_2NCS_2^-$) has continued to gain attention in the last decades. Dithiocarbamate anions constitute an important class of ligands and can easily be isolated as alkali metals or ammonium salts by reacting an amine with carbon disulfide (CS_2) in the presence of a base [5]. Further reaction of it with metal salts results in the formation of the corresponding metal dithiocarbamates. Dithiocarbamato ligands contain two soft sulfur atoms which can bind to the metals in a monodentate, bidentate, anisobidentate or triconnective fashion (Scheme 1) [6].

These ligands can often generate a broad variety of molecular and supramolecular structures [7]. In addition to their peculiar structural diversities, these ligands and their metal complexes have attracted attention as potential candidates for various applications in material science. For example, they are used as single-source precursors for the preparation of metal sulphides as thin films or nanoparticles [8–10]. A variety of dithiocarbamato metal complexes of transition metals and lanthanides have been prepared and used as precursors for the synthesis of metal sulphides [11–13]. These ligands also play an active role in medical science [14–16]. However, the chemistry of dithiocarbamato derivative of main group elements is less widely explored compare to transition metals or lanthanides [6]. In this context, organotin dithiocarbamates continue to be the focus of recent research works.

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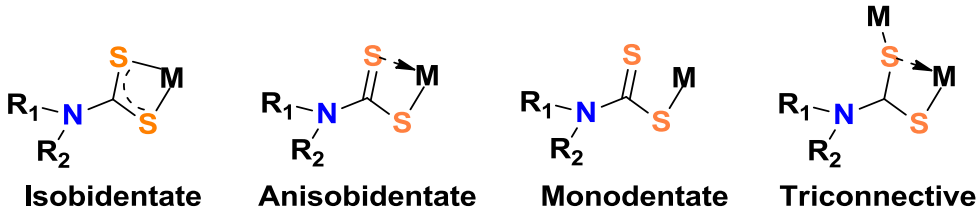
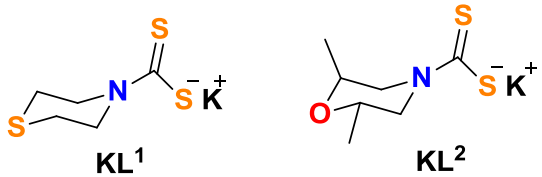


Scheme 1. Coordination modes of dithiocarbamate ligands.

Analogous to carboxylate derivatives, organotin dithiocarbamates generate a variety of structures [17]. Occasionally, they form macrocycle or supramolecular structures. For example, several 22-, 23-, 26- and 27-membered macrocyclic diorganotin(IV) bis-dithiocarbamates have recently been reported and few of them have been explored for their sensing abilities towards inorganic and organic anions [18,19]. Moreover, tin sulphides (SnS, SnS_2 and Sn_2S_3) which are synthesized from organotin dithiocarbamate complexes exhibit semiconducting properties with a band gap of 0.95–2.18 eV [20]. These sulphides are used as solar energy absorber, and in holographic recording and infrared detection [21]. In addition, organotin dithiocarbamates exhibit important biological activities such as anti-fungal, anti-microbial, anti-cancer activities etc [22]. For instance, organotin complexes of morpholine dithiocarbamate showed cytotoxic activity when tested against human HeLa and K562 tumor cell lines [23]. Moreover, it was found that these organotin complexes were more active than cisplatin. The antifungal activity of several organotin(IV) dithiocarbamates against *Candida albicans* (ATCC 18804), *Candida tropicalis* (ATCC 750) and resistant *Candida albicans* collected from HIV-positive patients was also tested [24]. A detailed application of organotin dithiocarbamate was documented by Tiekink [25]. However, the organotin moiety, organic substituents on the ligands and coordination number of the tin center play an active role in determining their biological activities [26]. Therefore, the design and synthesis of new organotin(IV) dithiocarbamate complexes by varying the organic groups on tin or the dithiocarbamato ligands has been a challenging task. During the last few years, we have been working on organotin compounds [27,28]. We are also working with dithiocarbamato ligands to prepare complexes of transition metals and lanthanides [29]. In continuation of our work, we have now chosen two dithiocarbamato ligands, potassium thiomorpholine-4-carbodithiolate (**KL^1**) and 2,6-dimethylmorpholine-4-carbodithiolate (**KL^2**) for the present study (Scheme 2).

These ligands have been reacted with various organotin compounds to prepare six organotin(IV) dithiocarbamate complexes [Ph_3SnL^1] (**1**), [$Bu_2Sn(L^1)_2$] (**2**), [$Ph_2Sn(L^1)Cl$] (**3**), [$Ph_2Sn(L^1)_2$] (**4**), [$Ph_2Sn(L^2)_2$] (**5**) and [$Ph_3Sn(L^2)$] (**6**). All ligands and complexes were characterized by multinuclear NMR spectroscopy and FT-IR spectroscopy. Moreover, the solid-state molecular structures of complexes **1**–**6** were determined by single-crystal X-ray diffraction analysis. The optical properties, thermal stability and antimicrobial activity of all complexes are documented.



Scheme 2. Potassium salts of thiomorpholine-4-carbodithiolate (**KL^1**) and 2,6-dimethylmorpholine-4-carbodithiolate (**KL^2**).

2. Experimental

2.1. Materials and analytical techniques

All reactions were executed under aerobic conditions. Starting materials were used as received from Aldrich (thiomorpholine, 2,6-dimethylmorpholine and dibutyltin dichloride), Acros organics (triphenyltin chloride), Alfa aesar (diphenyltin dichloride) and Merck (carbon disulfide) without any further purification. Solvents were distilled prior to use. Carbon, hydrogen and nitrogen microanalyses were carried out on a Thermo Scientific (FLASH 2000) CHNS elemental analyzer. FT-IR spectra were recorded in the solid state (ATR mode) using a Perkin Elmer- Spectrum RX-IFTIR spectrometer in the region of 4000–400 cm^{-1}. The electronic spectra of **1**–**6** were recorded on a Shimadzu UV-1800 spectrometer. ^1H, $^{13}C\{^1H\}$, $^{119}Sn\{^1H\}$ NMR of the complexes in solution were recorded on an FT NMR Spectrometer, Avance II (Bruker, 400 MHz). Thermogravimetric analyses were carried out using a Perkin Elmer, Diamond TG/DTA.

2.2. Procedure for the syntheses of ligands *KL^1* and *KL^2*

2.2.1. Synthesis of *KL^1*

A solution of thiomorpholine (1.002 mL, 10 mmol) in methanol (5 mL) was cooled in an ice bath. A cold solution of potassium hydroxide (0.561 g, 10 mmol) in H_2O-MeOH (10 mL, 1:1) was added to it. After stirring 15 min, an ice cold solution of carbon disulfide (0.604 mL, 10 mmol) in methanol (5 mL) was added maintaining the reaction temperature below 10 °C. A solid did appear which was stirred for 2 h, filtered and washed with cold methanol followed by drying in vacuum. The ligand was air stable and soluble in methanol at room temperature (25 °C). Yield (89%, 1.934 g): IR (ATR, cm^{-1}) ν = 1450 (C-N), 993 (C-S). ^1H NMR (DMSO, 400 MHz): δ = 2.52 (4H, t, S-CH_2), 4.59 (4H, t, N-CH_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, DMSO): δ = 26.5 (C-S), 51.7 (C-N), 213.8 (CS_2) ppm.

2.2.2. Synthesis of *KL^2*

Ligand **KL^2** was synthesized following same procedure as **KL^1**. Here, 2,6-dimethylmorpholine (1.232 mL, 5 mmol) was used instead of thiomorpholine. Yield (86%, 1.974 g). The ligand **KL^2** was white in color, air stable and was soluble in methanol at room temperature (25 °C). IR (ATR, cm^{-1}) ν = 1448 (C-N), 952 (C-S).^1H NMR (400 MHz, DMSO): δ = 1.06–1.08 (6H, m, CH_3), 2.39 (2H, m, N-CH), 3.36 (2H, m, N-CH), 5.80 (2H, m, O-CH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, DMSO): 18.6 (CH_3), 47.1(N-CH_2), 54.6 (N-CH_2), 68.7 (C-O), 70.8(C-O), 213.6 (CS_2) ppm.

2.3. General procedure for the syntheses of complexes *1*–*4*

To a solution of **KL^1** (0.1 g, 0.5 mmol) in methanol (5 mL), a solution of organotin(V) chloride in methanol (5 mL) was added. A white precipitate was immediately observed, which was stirred for 2 hrs. Thereafter it was filtered, washed with cold methanol and