



Anion interaction with homoditopic chlorodiorganotin(IV) dithiocarbamate complexes derived from a naphthalene diimide. A pathway to obtain metallomacrocycles

Nadia Alejandra Rodríguez-Uribe^a, Miguel Ángel Claudio-Catalán^b, Felipe Medrano^c, Georgina Pina Luis^d, Hugo Tlahuext^a, Carolina Godoy-Alcántar^{a,*}

^a Centro de Investigaciones Químicas, IICBA, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001, C. P. 62209 Cuernavaca, Morelos, Mexico

^b Departamento de Ciencias Químico-Biológicas, Instituto de Ciencias Biomédicas, Universidad Autónoma de Ciudad Juárez, Ciudad Juárez, Chihuahua, México

^c Departamento de Ciencias Químico Biológicas, Universidad de Sonora, Sonora, Mexico

^d Centro de Graduados e Investigación en Química del Instituto Tecnológico de Tijuana, Tijuana, Baja California Norte, Mexico

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ABSTRACT

Four new homoditopic *bis*[chlorodiorganotin(IV) and triorganotin(IV) dithiocarbamate] complexes derived from naphthalene diimide (NDI) with general formula $\text{NDI}-[(\text{CH}_2)_2\text{-N}(\text{CH}_2\text{Ph})(\text{CS}_2\text{SnR}_2\text{X})]_2$, **3**: R = *n*-Bu, X = Cl; **4**: R = Me, X = Cl; **5**: R = Ph, X = Cl; **6**: R = X = Me; were prepared from triethylammonium ((1,3,6,8-tetraoxo-1,3,6,8-tetrahydrobenzo[*lmn*][3,8]phenanthroline-2,7-diyl)bis(ethane-2,1-diyl))bis(benzyl-carbamodithioate) **2**. All compounds were characterized by IR, as well as ¹H and ¹³C NMR spectroscopy. The complexes **3–6** also were characterized by ¹¹⁹Sn NMR spectroscopy. In addition, complex **3** was further characterized by single-crystal X-ray diffraction analysis. The crystallographic study performed on complex **3** showed that the tin atom has a coordination geometry intermediate between square-pyramidal and a trigonal-bipyramidal, with τ value of 0.69. In addition the presence of cooperative C–H... π , C–H...S, C–H...O and S... π intramolecular interactions in the crystal structure of **3** was observed. The interaction of complexes **3–6** with anions (CH_3CO_2^- , F^- , H_2PO_4^-) in CDCl_3 was studied by UV/Vis, fluorescence and ¹¹⁹Sn NMR titrations. The addition of the foregoing anions to complexes **3–6** lead to the displacement of the chloride ligand at the tin(IV) atom. However, an the excess of F^- or H_2PO_4^- induced the self-assembly of complexes **3** and **5** in their corresponding binuclear metallomacrocycles.

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1. Introduction

Naphthalene diimides (NDIs) have widespread applications in biology, medicine, supramolecular chemistry and materials science. For instance, NDIs have been used to develop metal-free *n*-type semiconductors for electronic devices. Moreover, NDIs have been used as DNA intercalators, chemotherapy drugs, conducting as well as fluorescent materials, and chemical sensors [1]. Structurally, NDIs have a planar three-dimensional molecular arrangement having high π -acidity, which make them ideal for π - π stacking. In addition, the molecular structure of NDIs is easy to modify, by the introduction of functional groups to both the aromatic rings and the nitrogen atoms. The latter allowed for the fine-tuning of the chemical and molecular properties at the NDI-scaffold.

Dithiocarbamates (*dtcs*) are versatile ligands that easily bind a wide range of metal ions, which make them attractive motifs to convert NDIs into chemical sensors, molecular switches or coordination complexes with new properties. In addition, bifunctional dithiocarbamates have been used as platforms for the synthesis of metallomacrocycles and other supramolecular entities. For instance, Beer and coworkers synthesized metallomacrocycles employing *bis*-dithiocarbamates and either Cu(II) or Zn(II) as metal centers, and studied their properties for molecular recognition [2,3]. Later, Singh and coworkers prepared Ni(II)-, Zn(II)- and Cd(II)-metallomacrocycles from *bis*-dithiocarbamates by self-assembly. The resulting bimetallic complexes showed semiconductor behavior and were also applied for host-guest chemistry [4].

In addition to the afore said studies, our research group has demonstrated the use of *bis*- and *tris*-dithiocarbamates and organometallic tin(IV)-centers for the synthesis of a wide range of two- and three-dimensional metallomacrocycles [5–9]. Moreover, we have studied the application of this type of organometallic

* Corresponding author.

E-mail address: cga@uaem.mx (C. Godoy-Alcántar).