

Anion-assisted self-assembly of chlorodiorganotin (IV) dithiocarbamate derived from naphthylimide

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Abstract

Two new chlorodiorganotin(IV) dithiocarbamate complexes with general formula $\{(R_2SnCl)dtc\}$ ($dtc = R^1R^2NCS_2^-$, $R^1 = Bn$, $R^2 =$ naphthylimide; **3**, $R = n-Bu$; **4**, $R = Ph$) have been prepared from sodium *N*-[2-(benzylamino)ethyl] naphthalene-1,8-dicarboximide dithiocarbamate **2**. The *bis*-dithiocarbamate **3d** ($R_2Sn(dtc)_2$, $R = n-Bu$) was obtained as the thermodynamic product during the titration process (*vide infra*). All compounds were characterized by mass spectrometry, IR, 1H and ^{13}C NMR spectroscopy. The chlorodiorganotin(IV) dithiocarbamate complexes **3-4** also were characterized by ^{119}Sn NMR spectroscopy and single crystal X-ray diffraction analysis. The crystallographic study of these complexes showed the existence of C-H... π , S... π and π ... π intramolecular interactions, indicating that the naphthylimide aromatic fragment stabilized the complexes. Complexes **3** and **4** were studied as host for anions ($CH_3CO_2^-$, F^- , $H_2PO_4^-$) in $CDCl_3$ by UV/Vis and ^{119}Sn NMR spectrometric titrations. The tested anions cause the displacement of the chloride ligand of the metallic centre. The excess of F^- or $H_2PO_4^-$ induce the self-assembly of diorganotin(IV) dithiocarbamate to *bis*-dithiocarbamates $R_2Sn(dtc)_2$ (**3d**) instead of the breaking of the S-Sn covalent bond. Quantum mechanical calculations at DFT level (B3LYP/def2-TZVP) were performed to obtain the thermodynamic parameters of the reactions involved in the anion addition to the complexes.