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Microwave Assisted Stereoselective Synthesis of Cis-Substituted Tin^{IV} Phthalocyanine Dicarboxylates. Application as Corrosion Inhibitors[†]

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Two PcSn^{IV} dicarboxylate molecules were obtained through efficient microwave methodology with the aim to test them as corrosion inhibitors in the oil industry. The compounds were characterized by elemental analysis, IR, UV–vis, ^{1}H, ^{13}C NMR, and X-ray diffraction. The relative configuration of the two carboxylates is cis, placing the fatty acid moieties on the same face of the phthalocyanine macrocycle. In the solid-state the tin atoms possess square antiprismatic octacoordinated geometries. Both tin phthalocyanines were tested as corrosion inhibitors for hydrogen sulfide corrosive media showing a chemisorption process of the nanocap motifs on the metallic surface. Apparently, the length of the hydrophobic chain contributes significantly to the inhibition efficiency, in the sense that shorter chains increase the efficiency.

Complexes between metal ions and the phthalocyanine (Pc) macrocycle are reported for about 69 elements in the periodic table.[1] Since the structural arrangement of metallophthalocyanines (MPc) is determined by the size and location of the metal center with respect to the mean plane of the aromatic Pc^{2-} ligand, several conformations are known.[1] Those have been named according to their molecular shape, and the most common conformations are planar, ruffled, waved, domed, and skew domed.[1] Because Pcs reach nanometer dimensions, we prefer to describe all previous mentioned conformations, with metal displacement characteristic, as nanocap motifs in the scope of this Communication.

The first X-ray elucidated tin Pc, containing an eight-coordinated tin atom, was Pc$_2$Sn^{IV}, where the two Pc^{2-} units coordinate to the metallic center yielding a sandwich type complex.[2]

Our current interest in the design of new SnPc complexes with potential applications in materials science stems from our previous work in the field of tin chemistry,[3] and from the more recent developments of synthetic Pc chemistry,[4] particularly those concerned with obtaining soluble materials. In addition it is well-known that X-ray structures of Pc molecules are seldom found.[1,4–7]

In our efforts to develop new corrosion inhibitors, we became interested in cis-substituted tin^{IV} phthalocyanine dicarboxylates,[8] which have not been used for this purpose so far.[9] Three factors were considered important to select SnPc complexes as subjects of study: (i) SnPc dicarboxylates have inherent thermal and kinetic stability and, therefore, can endure harsh reaction conditions;[4–6] (ii) a variety of

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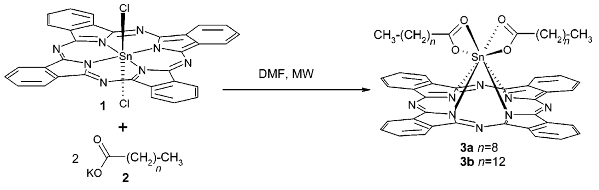
Scheme 1. Stereoselective Reaction Pathway Leading to the Formation of PcSn^{IV}(carboxylate)$_2$ Derivatives



carboxylate ligands are commercially available, including those functionalized with long aliphatic chains (fatty acids) and with arylic moieties (this allows one to modulate the hydrophobic−hydrophilic character of the organic substituents on the metal ion to achieve surface protection); and (iii) cis-substitituted SnPc derivatives with a domelike conformation possess an extended π-electron system face of nanometer dimensions (=nanocaps). This electron rich face would be used as a reagent for acid−base reactions on the metal surfaces to protect them.[1,4−6] Unfortunately, one factor that restricts the use of tin^{IV} phthalocyanine derivatives for industrial purposes is their elevated cost. Therefore, we undertook an effort to optimize the preparation of tin^{IV} phthalocyanine dicarboxylates, using microwave-assisted synthetic methods, which are known to give higher yields and cleaner products.[10]

Herein, we report our preliminary results of the stereoselective, microwave-assisted synthesis of cis-substituted tin^{IV} phthalocyanine dicarboxylates and their application as corrosion inhibitors for steel. It is noteworthy that there is only one report on the structural characterization of a tin^{IV} phthalocyanine dicarboxylate.[8]

PcSn^{IV}Cl$_2$ **1** was prepared following a modification of Kroenke's methodology.[11] In a typical reaction the starting materials were heated for 10 min in a 600 W focused-microwave oven using quinoline as solvent. The crude reaction product was washed repeatedly with ethanol and dried at room temperature with reduced pressure to give a dark blue crystalline solid in 85% yield. Compound **1** and the potassium salts of capric (**2a**) and myristic (**2b**) acids were combined in DMF using a 1:2 molar ratio. The mixture was heated in the microwave oven for 10 min to yield PcSn^{IV} dicarboxylates **3a** and **3b** (Scheme 1). Longer reaction times led to partial decomposition of **3a** and **3b** to dicyanobenzene, as demonstrated by ^{1}H and ^{13}C NMR experiments. On the other hand, if the reaction times were shortened, completeness of the reaction was not achieved. With 300 W of microwave power lower yields were obtained for the same exposure periods. The desired products were separated from the potassium chloride formed during the reaction by filtration. Evaporation of the solvent and recrystallization from methanol gave metallic blue powders of **3a** and **3b** in 76% and 83% yield, respectively, which are excellent yields compared to previously reported syntheses.[8,10] Elemental analysis, IR, UV−vis, and ^{1}H, ^{13}C, and ^{119}Sn (1D and 2D) NMR measurements permitted the complete characterization of the final products.

The IR data provide useful information on the binding mode of the carboxylate ligands to the tin atoms. For previously reported metalloporphyrin (MPorph) systems with σ-bonded CH$_3$COO$^-$ fragments (M = Ge and Sn)[12] the ν_{as}(COO) and ν_s(COO) vibrations appear at 1678−1661 cm^{-1} and 1294−1269 cm^{-1}, respectively. In contrast, for MPorph systems with μ ligation (M = In and Tl)[12] the ν_{as}(COO) and ν_s(COO) bands appear at approximately 1562−1556 cm^{-1} and 1421−1412 cm^{-1}. The IR spectra of compounds **3a** and **3b** show the ν_{as}(COO) and ν_s(COO) bands at 1609 cm^{-1} and 1422−1418 cm^{-1}, respectively, indicating a coordination mode intermediate between a σ and μ ligation, known as anisobidentate coordination mode.

The ^{1}H NMR spectra for **3a** and **3b** show triplets for the α −CH$_2$− protons at δ = 0.52 ppm, well-defined pseudoquintets for the following three −CH$_2$− groups at δ = 0.14, 0.37, and 0.79 ppm, and triplet signals at δ = 1.19 ppm for the −CH$_3$ groups at the end of the tail. The signals for the first four −CH$_2$− groups are shifted considerably to low frequencies and give evidence for an anisotropic shift caused by a polarized current on both sides of the Pc^{2-} macrocycle.

Complete ^{13}C and ^{119}Sn NMR spectra could only be obtained with relaxation times of at least 3 s. With shorter relaxation times neither the carboxylic group nor the tin signals were detected, indicating a fixed μ-coordination of the RCOO$^-$ group to the Sn atom. This lessens the contribution of the spin-rotational relaxation mechanism.[13] The ^{119}Sn NMR chemical shifts at −845.9 ppm for **3a** and −846.4 ppm for **3b** are the lowest frequency signals reported so far for Sn^{IV} complexes and indicate therefore octacoordinated tin atoms in solution for the present compounds.[14] More negative ^{119}Sn NMR shifts have been observed only in some tin alloys due to a larger spin−orbit contribution.[15]

The X-ray structures of **3a**[16] and **3b**[17] show that the chlorine−carboxylate ligand exchange during the course of the reaction results in an overall change in configuration from trans to cis (Scheme 1, Figures 1 and 2).[18] In both cases, the Pc^{2-} ligand is significantly distorted from planarity and the resulting conformations are a ruffled nanocap for **3a** and a half-domed nanocap for **3b**. The Sn−N bond lengths are 2.148(2), 2.158(2), 2.181(2), and 2.186(2) Å for **3a**, and 2.143(5), 2.154(5), 2.183(5), and 2.206(5) Å for **3b** (the sum of the van der Waals radii for Sn and N is 3.72 Å[19]). The

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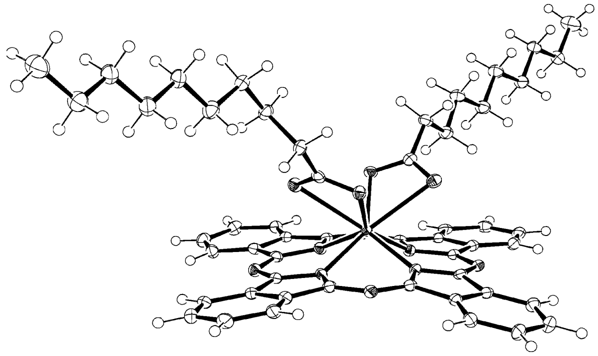

Figure 1. Molecular structure of **3a**.

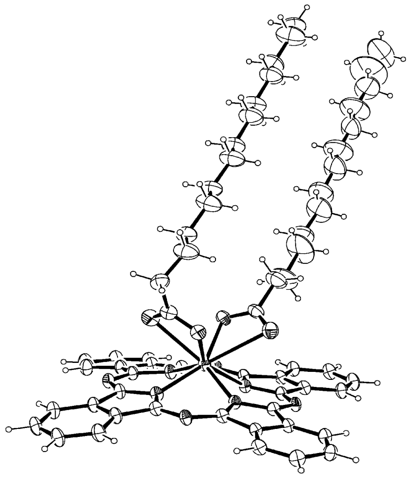

Figure 2. Molecular structure of **3b**.

presence of the $(RCOO)_2Sn$ moiety induces a deformation of the Pc^{2-} ligand, which is directly responsible of the elongation of the N−Sn bonds. This, in turn, allows the coordination number to increase, yielding the hypercoordinated compounds with a nanocap shape.[1,7,8] The displacements of the tin atoms from the N_4 core are 0.956(1) Å for **3a** and 0.957(3) Å for **3b**. The hydrocarbon chains in the capric acid derivative **3a** are oriented in opposite directions (Figure 1). However, in the myristic acid derivative **3b** (Figure 2) they have a parallel arrangement. At present we are preparing a homologous series of complexes to evaluate the effect of hydrocarbon chain length on conformation.

Table 1. LPR Electrochemical Data for **3a** and **3b** at 500 ppm

corrosion inhibitor	reference	**3a**	**3b**
R_p [ohm]	2.78×10^2	2.50×10^3	1.00×10^3
I_{corr} [A]	9.18×10^{-5}	2.24×10^{-5}	3.52×10^{-5}
E_{corr} [V/SCE]	−0.51	−0.46	−0.49
efficiency [%]	0.00	75.58	61.61

As already indicated by the IR information, the carboxylate groups are asymmetrically μ-ligated, and this is corroborated by the X-ray data, which show two pairs of different tin−oxygen bond lengths for both compounds. The σ Sn−O bond distances are 2.104(2), 2.102(2) Å for **3a**, and 2.101(5), 2.100(4) Å for **3b**, while the Sn···O bond distances are 2.545(2), 2.627(2) Å for **3a**, and 2.627(6), 2.691(6) Å for **3b** (the sum of the vdW radii for O and Sn is 3.69 Å[19]). Examination of the Fourier density maps revealed ring points for the −O−C═O···Sn− moieties denoting the presence of a four-membered ring. The dihedral angles for the −O−C═O···Sn− moiety are −1.4° and −0.8° for **3a** and −0.2°and 6.4° for **3b**. They provide further evidence for the existence of octacoordinated tin atoms. As far as we know, this is the first series of *cis*-substituted tin^{IV} phthalocyanine dicarboxylates with an N_4O_4 core. The coordination geometry of the tin atom is approximately square antiprismatic.[1]

Compounds **3a** and **3b** were tested as corrosion inhibitors for hydrogen sulfide corrosive media at 500 ppm.[9] The electrochemical technique employed to measure inhibition efficiencies was the linear polarization resistance (LPR) using the Tafel relationship.[9b] Working electrodes were made of SAE-1018 steel, and the corrosion process was emulated with a potential applied to the electrochemical cell contents. The corrosion inhibition efficiencies measured for **3a** and **3b** are 75.6% and 61.6%, and they are attributed to a chemisorption process of the $PcSn^{IV}$ dicarboxylate molecules on the metallic surface. Apparently, the length of the hydrophobic chain contributes significantly to the inhibition efficiency, in the sense that shorter chains increase the efficiency (Table 1). As we mentioned before, we are preparing a full series of fatty acid derivatives to clarify this behavior.

In summary, this Communication has shown that *trans*-$PcSn^{IV}$ dichloride is transformed stereoselectively to *cis*-$PcSn^{IV}$ dicarboxylates. Using a microwave assisted preparative method the reaction is accelerated at least 15 times compared to a conventional thermal reaction and gives higher yields. The results show that the cis configuration of these complexes, with an electron rich naked face, makes them interesting molecules as corrosion inhibitors, e.g., for hydrogen sulfide aggressive media. These molecules might also be interesting for other fields of surface chemistry, catalysis, and supramolecular chemistry.

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Supporting Information Available: CIF files for the structural analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Crystal data for **3a**: triclinic; $P\bar{1}$; $a = 13.1764(9)$ Å, $b = 13.4184(9)$ Å, $c = 14.9293(10)$ Å, $\alpha = 65.399(1)°$, $\beta = 71.356(1)°$, $\gamma = 78.930(1)°$; $V = 2268.7(3)$ Å^3; $T = 100(2)$ K; $R1 = 0.0373$ ($I < 2\sigma(I)$), 0.0423 (all data); $wR2 = 0.0836$ ($I < 2\sigma(I)$), 0.0864 (all data); GOF = 1.037. Tables of crystallographic parameters, atomic coordinates, anisotropic thermal parameters, bond distances, bond angles as well as a list of the structural factors have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 215862 for **3a**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, 44-1223-336033; e-mail, deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

(17) Crystal data for **3b**: triclinic; $P\bar{1}$; $a = 9.559(5)$ Å, $b = 11.670(5)$ Å, $c = 25.913(5)$ Å, $\alpha = 81.983(5)°$, $\beta = 89.708(5)°$, $\gamma = 73.359(5)°$; $V = 2740.7(19)$ Å^3; $T = 293(2)$ K; $R1 = 0.0695$ ($I < 2\sigma(I)$), 0.1042 (all data); $wR2 = 0.1427$ ($I < 2\sigma(I)$), 0.1580 (all data); GOF)= 1.162. General crystallographic information, has been deposited with the Cambridge Crystallographic Data Center, CCDC No. 215863 for **3b**.

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