Syntheses, density functional and sparkle PM6 semi empirical theoretical studies of O,O′-dialkyl/alkylenedithiophosphate derivatives of tin(IV) phthalocyanine adducts

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ABSTRACT

Seven new PcSn [$S_2P(OR)_2$]$_2$ and PcSn [$S_2P(OGO)_2$]$_2$ tin complexes where Pc is phthalocynine, R = Et, n-Pr, ios-Pr and tert-Bu and G = $CH_2CMe_2CH_2$, $CH_2CEt_2CH_2$, and CMe_2CMe_2 were synthesized and characterized by elemental analyses, Molecular weight determinations, IR and ^{31}P spectroscopy. A sudden novel PcSn [$SP(OR)_2O$]$_2$ where R = iso-Pr has been recovered upon the hydrolysis of the complex with R = iso-Pr during recrystallization. Microanalytical and ^{31}P NMR data revealed a 1:2 metal-ligand (O,O′-dialkyl and alkylenedithiophosphate) molar ratio in all complexes. Geometries were fully optimized at the B3LYP functional where the basis sets used were specified as generic basis sets and geometrical structures and electronic properties of the complexes were evaluated. The optimized geometries were confirmed to be minima on the potential energy surfaces through frequency calculations. The validity of the employed level of theory has been established through comparison of the calculated geometrical parameters of **12** with their observed counterparts. Thermodynamic stabilities were assessed through energy calculations. Aromaticity indices, local softnesses and condensed Fukui Functions were evaluated utilizing the optimized geometries at the specified level of theory. The absorption spectra of the complexes have been established using ORCA2.9 package utilizing the predicted optimized wave functions. Complexes proved to have high electronic susceptibilities.

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1. Introduction

Phthalocyanine has been accidently synthesized as a by-product early in the twentieth century [1] and as a copper salt two decades later [2]. Ever since, interests have been dramatically increased with phthalocyanine and its derivatives [3–13].

Colorant phthalocyanine is a hetero dianionic macro cyclic porphyrin like compound, consists of four isoindole $C_6H_4C_2N$ units linked by four nitrogen atoms to form a high chemically stable, symmetrical, planar and conjugated chain, where various different metal ions and some metalloids could be hosted in its center.

Phthalocyanines are one of the promising compounds due to the possibility of application in electro-optic devices, photoconducting agents, photovoltaic cell elements, nonlinear optics, electro-catalysis and other photoelectronic devices [4].

Metal complexes containing phthalocyanine where the metal is Ge [5], Cr, Fe, Cu, Co, Ni, Al, Si, Ga, Sn, U [6,7], Ti, W, Mo [8], Nb [9] or Zn was the field of many studies particularly in the last few decades. ZnPc derivatives are among the most important ones of the phthalocyanine complexes [3,5]. They are of particular interests due to their unique photosensitizing properties for photodynamic therapy (PDT) [6], magnetic circularly polarized luminescence (MCPL), absorption and magnetic circular dichroism (MCD) spectra. Recently, SnPc derivatives received an increasing attention due to its potential as corrosion inhibitors [7–13].

In this paper a new O,O-dialkyl/alkylenedithiophosphate

derivatives of phthalocyanine tin (IV) will be presented and identified by elemental analysis, molecular weight determination,^{31}P NMR FT-IR and X-ray single crystallography when possible. Additionally, the prepared SnPcs complexes will be theoretically investigated by the use of density functional theory and sparkle PM6 semiempirical level of theories to shed the light on their geometries, electronic properties and aromaticity indices. Fukui Functions will be estimated in attempt to rationalize the hydrolysis outcome of the prepared complexes.

2. Experimental work

2.1. Syntheses and characterization

Stringent precautions were taken to exclude moisture during experimental manipulation. Dialkyl and alkylenedithiophosphoric acids were prepared according to reported procedures [14]. Tin(IV) phthalocyanine dichloride was used as it is, (Sigma-Aldrich, 97.0% purity). IR spectra were recorded as Nujol mulls using CsI cells in the region 200-4000 cm^{-1} on an FT-IR 8201 PC spectrometer. [1]H and ^{13}C spectra were recorded on a Jeol-FT NMR spectrometer-LA300 and using TMS as the internal reference. ^{31}P NMR spectra were recorded in $CHCl_3$ using H_3PO_4 as an external reference on the same instrument. Elemental analysis for carbon, hydrogen, and nitrogen were carried out using EA 1110-CHNS Elemental Analyzer (CE Instrument). Messenger's method [15] was employed for Sulfur determination utilizing barium sulfate. Tin was estimated gravimetrically as tin oxide. Molecular weight determinations have been accomplished using the freezing point depression technique.

Several O,O′-dialkyl/alkylenedithiophosphate derivatives of tin (IV) Phthalocyanine were prepared in 85—95% yields by refluxing a slight excess (0.55 g, 2.13 mmol) of the sodium salt of the appropriate O,O′-dialkyl/alkylenedithiophosphoric acid with (0.74 g, 1.068 mmol) tin (IV) Phthalocyanine dichloride in 70 ml of benzene for 5 h with constant stirring. Polar solvents such as CH_2Cl_2 [16,17] could be used instead of benzene in preparation of such complexes. The dark purple color of the tin (IV) phythalocyanine dichloride changed to light greenish color through the reaction progress. To monitor the progress of reactions and to establish the identity and purity of reactants and products, thin layer chromatography was performed on aluminum slides coated with silica gel 60, using appropriate solvent systems and the spots were visualized under ultra-violet light. The Sodium chloride was removed by filtration while the solvent excess was removed under vacuum. The products were washed repeatedly with n-hexane and hydrolyzed by water, then dried under vacuum. Then n-hexane (approximately 5 mL) was added to benzene solution of the solid compounds and left in the refrigerator overnight in open file at 4 °C for 2—3 days. Suitable Crystals of only $C_{32}H_{16}N_8Sn$ [$(CH_3)_2CHO)_2POS]_2$ for X-ray crystallography was obtained, washed with n-hexane and dried under vacuum (red crystals). We could not get crystals in dry conditions. The crystals showed stability at room temperature, and in common nonpolar organic solvents such as benzene. They also showed slight solubility in heated polar solvents such as ethanol.

2.2. Crystallographic analysis

A red needle-shaped crystal with dimensions $0.29 \times 0.07 \times 0.03$ mm^3 was mounted on a nylon loop with paratone oil. Data were collected using a Bruker APEX-II CCD diffractometer equipped with Oxford Cryo systems low-temperature device, operating at $T = 173$ (2) K. Data were measured using ω of $-0.50°$ per frame for 29.94 s using MoKα radiation (sealed tube, 50 kV, 40 mA). The total number of runs and images was based on

the strategy calculation from the program COSMO-V1.61 [18]. The actually achieved resolution was $\Theta = 25.335$. Cell parameters were retrieved using the SAINT-V8.34A-2013 [19] software and refined using SAINT (Bruker, V8.34A, 2013) on 8677 reflections, 24% of the observed reflections. Data reduction was performed using the SAINT (Bruker, V8.34A, 2013) software which corrects for Lorentz polarization. The final completeness is 100.00 out to 25.335 in Θ. The absorption coefficient μ of this material is 0.801 at this wavelength ($\lambda = 0.71073$) and the minimum and maximum transmissions are 0.8176 and 1.0000. The structure was solved in the space group $P2_1/c$ (# 14) by Charge Flipping using the Olex2. solve [20] structure solution program and refined by Least Squares using version of XL (Sheldrick, 2008) [21]. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model, except for the Hydrogen atom on the nitrogen atom which was found by difference Fourier methods and refined isotropically. The structure was refined by Least Squares using version 2014/6 of XL [19] incorporated in Olex2 [22]. The crystal data of bis(O,O′-di-isopropyldithiophosphato)tin (IV) phth-alocyanine are summarized in Table 1.

2.3. Computational details

The gaseous phase ground state molecular structures of all adducts in the study were fully optimized at the density functional of Becke exchange functional and the correlation functional of Lee, Yang and Parr (DFT/B3LYP) [23,24] and at the Semiempirical Sparkle PM6 level of theories implemented in the Gaussian package for the sac of comparison. The B3LYP calculation was performed with the aid of the gen key word in the route sentence to allow specified basis sets to be used in the Gaussian calculations. Sophisticated 6-31G basis set was used to optimize each of the carbon, hydrogen, nitrogen and oxygen atoms. The third row elements; sulfur and phosphorous, were optimized at the Dunning's correlation consistent quadruple zeta with the inclusion of diffused d functions; cc-pvqz + d basis set, while the 3—21 g basis set was employed to model the Sn moiety. Analytical vibrational frequencies were conducted using second-derivative computations at the fully optimized geometry to obtain zero-point vibrational energy (ZPVE) corrections. Aromaticity indices, local softnesses and the condensed Fukui Functions f^- and f^+ which correspond to nucleophilic and electrophilic attack, respectively, were calculated at the B3LYP/6-31G level of theory. Singlet excited states were modeled using the CIS/TD-DFT (B3LYP)/6-31G(d) using ORCA2.9 package [25,26] and visualized with Gabedit software [27]. Electronic properties of the fully optimized geometries are calculated using MOPAC 2016 [28].

The Gaussian 09 series [29] of programs employed for ab initio calculations were run at King Abdulaziz University's High Performance Computing Center (Aziz Supercomputer) (http://hpc.kau.edu.sa/). Visualization of structures has been accomplished by the aim of Gauss View [30] and Chemcraft [31] programs. Crystallographic data resolved from the X-ray cif file has been visualized using Hg-Mercury software [32].

3. Results and discussions

3.1. Micro analytical results

Experimental details such as physical properties, molecular weights of the isolated O,O-dialkyl/alkylenedithiophosphatetin (IV) phthalocyanine adducts, elemental analyses of their hydrogen, carbon, sulfur and tin contents as well as ^{31}P NMR data are recorded in Table 2.