

## Novel Tin Complexes Containing an Oximato Ligand: Synthesis, Characterization, and Computational Investigation

by **Raji Thomas<sup>a)</sup>**, **Joseph P. Nelson<sup>a)</sup>**, **Ramchand T. Pardasani<sup>b)</sup>**, **Pushpa Pardasani<sup>\*a)</sup>**,  
and **Tulsi Mukherjee<sup>c)</sup>**

<sup>a)</sup> Department of Chemistry, University of Rajasthan, Jaipur-302055, India  
(e-mail: pushpa.pardasani@gmail.com)

<sup>b)</sup> Department of Chemistry, Central University of Rajasthan, Bandarsindri, Ajmer-305802, India

<sup>c)</sup> Chemistry Division, BARC, Mumbai-400085, India

---

Organotin complexes **1–6** of the general formula  $[\text{SnR}_2\text{L}]$  and  $[(\text{SnR}_3)_2\text{L}]$  ( $\text{L}$  = phenanthrenequinone dioximato – a bidentate ligand,  $\text{R}$  = Me, Bu, and Ph) were synthesized by the reaction of the sodium salt of the ligand  $\text{H}_2\text{L}$  (prepared *in situ* with MeONa) and  $\text{SnR}_2\text{Cl}_2/\text{SnR}_3\text{Cl}$  in 1:1 and 1:2 molar ratios. The physical and spectral properties of the newly synthesized complexes **1–6** are described. DFT and HF Calculations were performed to confirm the proposed structures.

---

**Introduction.** – Since *Ziese* synthesized in 1827 the first organometallic compound  $\text{K}[\text{PtCl}_3(\text{CH}_2=\text{CH}_2)]$  [1], the organometallic chemistry has grown enormously although most of its applications have only been developed in recent decades. Coordination chemistry of oxime precursors is a fascinating area which has attracted the attention of inorganic chemists due to its variety of versatile electronic distribution [2]. The chemistry of (vicinal-dioximato)metal complexes has been studied and has been the subject of several reviews [3]. Oxime ligands and oximato complexes show an impressively rich variety of reactivity modes which leads to various unusual types of chemical compounds. Coordination compounds of vicinal dioximes are interesting for many applications in a variety of high-technology fields, such as analytical reagents, as models for biological systems, in medicines, catalysis, electro optical sensors, liquid crystals, and trace metal analysis [4].

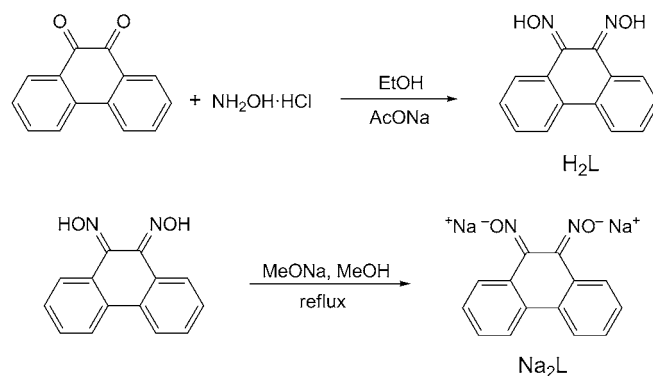
Organotin complexes of bidentate oxime ligands have been of great interest due to their pharmacological relevance. Because of the large size of the Sn-atom and availability of low lying empty 5d atomic orbitals, a coordination number greater than four is frequently encountered in organotin structures. Although organotin compounds have been known since the 1850s, the commercial application of organotin for the use as PVC stabilizers [5] in the 1940s promoted extensive studies in this area. Organotin(IV) complexes are put to use in various fields [6][7] and exhibit potential biological application such as insecticidal, fungicidal, and antitumor activities. N-, O-, and S-Donor ligands have been used to enhance the biological activity of organotin derivatives [8][9]. Also organotin compounds with N- and O-donor ligands have widely been tested for their possible use in cancer chemotherapy [10].

Thus, in view of the synthetic and pharmacological significance of organotin complexes and in continuation of our interest in organotin and organotitanium chelates

[11][12], we report herein the synthesis and spectrophotometric characterization of novel methyl-, butyl- and phenyltin complexes of 9,10-phenanthrenequinone dioxime (= phenanthrene-9,10-dione 9,10-dioxime). The structures of alkyl/aryl tin complexes can be either monomeric, dimeric [13], oligo- and polymeric [14], or cyclooligomeric which are mainly formed through intermolecular Sn ← O and Sn ← N bonds. Besides the synthesis, computational methods were applied to validate the proposed structures and determine the structural parameters.

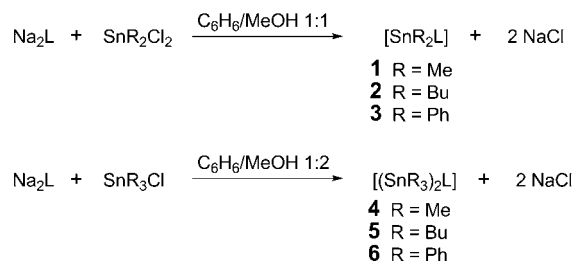
**Results and Discussion.** – The ligand 9,10-phenanthrenequinone dioxime ( $H_2L$ ) was prepared by the reaction of the vicinal diketone with hydroxylamine hydrochloride in the presence of sodium acetate (*Scheme 1*). The dioxime was then converted to its sodium salt  $Na_2L$  by refluxing with sodium methoxide in methanol.

Scheme 1. Preparation of Ligand



The reaction of the sodium salt of  $H_2L$  with dichlorodialkyl- or dichlorodiphenylstannane and chlorotrialkyl- or chlorotriphenylstannane ( $\text{SnR}_2\text{Cl}_2$  and  $\text{SnR}_3\text{Cl}$ ) in 1:1 and 1:2 molar ratios, respectively, produced organotin complexes **1–6** of the general formula  $[\text{SnR}_2\text{L}]$  and  $[(\text{SnR}_3)_2\text{L}]$  (*Scheme 2*). Their structures (*cf. Fig. 1*) were established by spectroscopic means.

Scheme 2. Preparation of Complexes **1–6**



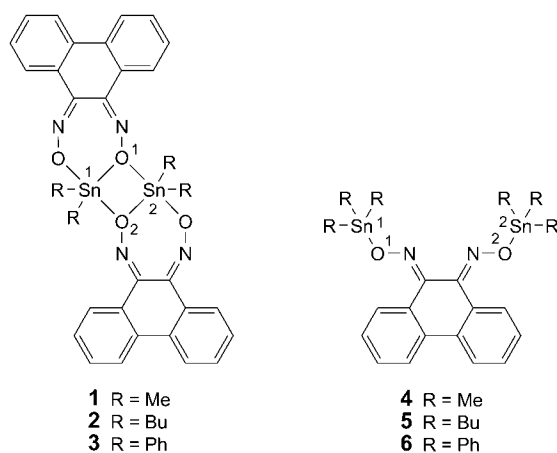


Fig. 1. Proposed structures of complexes **1–6**

In the IR spectrum of the ligand  $H_2L$ , no characteristic  $C=O$  absorption appeared at  $1675\text{ cm}^{-1}$  indicating the formation of the dioxime. The characteristic  $\tilde{\nu}_{(OH)}$  of the  $=NOH$  group and  $\nu_{(C=N)}$ , and  $\tilde{\nu}_{(NO)}$  stretching vibrations were observed at  $3140\text{--}3122$ ,  $1600$ , and  $951\text{ cm}^{-1}$ , respectively. The formation of the complexes **1–6** was ascertained by the disappearance of  $\tilde{\nu}_{(OH)}$  band as well as by the appearance of medium-intensity peaks in the regions  $524\text{--}570$  and  $485\text{--}570\text{ cm}^{-1}$  assignable to  $\tilde{\nu}_{(Sn-O)}$  and  $\tilde{\nu}_{(Sn-C)}$ , respectively [15] (Table 1). While the  $\tilde{\nu}_{(NO)}$  stretching vibrations of  $H_2L$  was shifted to slightly lower frequencies, the  $\tilde{\nu}_{(C=N)}$  stretching vibrations remained almost unchanged upon complexation. The low-frequency shift of the  $(N-O)$  vibration in the IR spectra of the tin(IV) complexes as compared to that of the ligand is an evidence for the coordination through O-atoms. There was no characteristic peak for  $Sn \leftarrow N$  which is usually observed in the region  $300\text{--}400\text{ cm}^{-1}$  [16].

The  $^1H$ -,  $^{13}C$ -, and  $^{119}Sn$ -NMR spectra of all the complexes **1–6** were recorded in  $CDCl_3$  and  $(D_6)DMSO$  (Table 1). In the  $^1H$ -NMR spectrum ( $(D_6)DMSO$ ) of the ligand  $H_2L$ , the exchangeable protons of the OH groups appeared as a *s* at  $\delta(H)$  12.24. On complexation, this signal disappeared indicating deprotonation of the  $=NOH$  groups and complexation with the tin metal, along with subsequent formation of  $Sn-O$  bonds. The resonances of the aromatic protons of the phenanthrene moiety of  $H_2L$  appeared at  $\delta(H)$  8.63–7.36 and remained almost unchanged in the complexes. The butyltin protons of **2** and **5** were observed in the region  $\delta(H)$  0.06–1.92: A well-defined *t* at  $\delta(H)$  0.933 was attributed to the Me protons of the butyl group, whereas the resonances of the  $CH_2$  protons were observed as *m* at  $\delta(H)$  1.131–1.747. The Me protons of the methyltin derivatives **1** and **4** appeared as *s* at  $\delta(H)$  0.43–0.38.

In the  $^{13}C$ -NMR spectrum of  $H_2L$ , the  $C=NOH$  group was observed at  $\delta(C)$  144.64; other signals in the range  $\delta(C)$  141.2–121.6 were assigned to the aromatic C-atoms. A downfield shift of the signals of different C-atoms on complexation confirmed the formation of complexes **1–6** with  $Sn-O$  bonds (Table 1). In complexes **2** and **5**, the butyl resonances in the range  $\delta(H)$  13.51–13.63 were assigned to the Me groups and those at  $\delta(C)$  28.05–32.88 to the  $CH_2$  groups [17]. Besides there was only a downfield

Table 1. Spectral Data of *Organo(oximate)tin(IV)*. Complexes **1–6**. IR Absorptions in  $\text{cm}^{-1}$ ; NMR signals  $\delta$  in ppm.

| Compound             | IR          | NMR ( $\delta$ )                          |  | $^{13}\text{C}$      | $^{119}\text{Sn}$ |
|----------------------|-------------|---|--|----------------------|-------------------|
|                      |             | $^1\text{H}$                              |  |                      |                   |
| <b>1<sup>a</sup></b> | 1595 (C=N), | 8.57–7.31 ( <i>m</i> , 8 arom. H),        |  | 145.52 (C=N),        | – 135.50          |
|                      | 570 (Sn–C), | 0.43 ( <i>s</i> , 2 MeSn)                 |  | 134.21–123.39 (C=C), |                   |
|                      | 548 (Sn–O)  |   |  | 1.02 (MeSn)          |                   |
| <b>2<sup>a</sup></b> | 1592 (C=N), | 8.57–7.64 ( <i>m</i> , 8 arom. H),        |  | 149.82 (C=N),        | – 137.70          |
|                      | 541 (Sn–C), | 1.92–0.80 ( <i>m</i> , 2 BuSn)            |  | 140.64–120.87 (C=C), |                   |
|                      | 547 (Sn–O)  |   |  | 32.88–13.51 (BuSn)   |                   |
| <b>3<sup>a</sup></b> | 1585 (C=N), | 8.65–7.27 ( <i>m</i> , 8 arom. H, 2 PhSn) |  | 150.74 (C=N),        | – 307.41          |
|                      | 558 (Sn–C), |   |  | 132.21–121.23 (C=C)  |                   |
|                      | 524 (Sn–O)  |   |  |                      |                   |
| <b>4<sup>a</sup></b> | 1594 (C=N), | 7.85–6.90 ( <i>m</i> , 8 arom. H),        |  | 146.69 (C=N),        | + 139.72          |
|                      | 510 (Sn–C), | 1.677–0.385 ( <i>s</i> , 3 Me)            |  | 129.30–121.32 (C=C), |                   |
|                      | 560 (Sn–O)  |   |  | 1.25 (MeSn)          |                   |
| <b>5<sup>a</sup></b> | 1590 (C=N), | 8.03–7.26 ( <i>m</i> , 8 arom. H),        |  | 150.46 (C=N),        | + 106.41          |
|                      | 485 (Sn–C), | 1.74–0.06 ( <i>m</i> , 3 BuSn)            |  | 131.68–123.01 (C=C), |                   |
|                      | 539 (Sn–O)  |   |  | 28.05–13.63 (BuSn)   |                   |
| <b>6<sup>b</sup></b> | 1588 (C=N), | 7.79–7.08 ( <i>m</i> , 8 arom. H, 3 PhSn) |  | 147.82 (C=N),        | – 254.21          |
|                      | 530 (Sn–C), |   |  | 139.61–123.38 (C=C)  |                   |
|                      | 570 (Sn–O)  |   |  |                      |                   |

<sup>a</sup>) IR in KBr, NMR in  $\text{CDCl}_3$ ; <sup>b</sup>) IR in KBr, NMR in ( $\text{D}_6$ )DMSO.

shift  $\Delta\delta(\text{C})$  of 3–4 of the C=N signal, thus confirming the absence of Sn ← N coordination.

The  $^{119}\text{Sn}$ -NMR chemical shifts of organotin compounds cover a range of 600 ppm. Besides, as the electron-releasing power of the alkyl group bonded to Sn in **1**, **2**, **4**, and **5** increased, the Sn-atom became more shielded, thus shifting the  $\delta(\text{Sn})$  towards higher field (*Table 1*). Even though Ph groups have a huge electron-withdrawing effect, upon replacement of the alkyl groups with the Ph group (see **3** and **6**), the  $\delta(\text{Sn})$  moved towards lower frequencies [18]. Another important factor about  $^{119}\text{Sn}$ -NMR is that the value of the  $^{119}\text{Sn}$ -NMR chemical shift is proportional to the coordination number of the central Sn-atom. Thus, the  $s$  at  $\delta(\text{Sn})$  139.72 and 106.41 of **4** and **5**, respectively, were diagnostic for a tetra-coordination of the Sn-atom suggesting the bonding of the deprotonated O-atom of the oxime groups to the Sn-atom. Complex **6** in ( $\text{D}_6$ )DMSO gave a signal at  $\delta(\text{Sn})$  –254.21, indicating that the Sn-atom was five-coordinated in solution due to the presence of coordinated solvent. In the  $^{119}\text{Sn}$ -NMR spectra of complexes **2** and **1** in  $\text{CDCl}_3$ , a sharp signal at  $\delta(\text{Sn})$  –137.70 and –135.50, respectively, was observed, both these chemical-shift values being in the range of a penta-coordinated Sn-atom, thus suggesting the formation of dimer complexes. In these complexes, one of the O-atoms from each monomer unit is involved in an ‘intermolecular’ bond (Sn ← O) and becomes tri-coordinate ( $\text{O}^1$ ,  $\text{O}^2$ ), while the other remains di-coordinate (O). The  $\delta(\text{Sn})$  of complex **3** at –307.41 was also in the range of penta-coordinated organotin chelates as given by *Otera* [19]. The more upfield value of **3** as compared to those of **1** and **2** was due to the presence of the Ph groups. Thus, it may be concluded that in 1:1 complexes, the Sn-atom is penta-coordinated, and in 1:2 complexes, the Sn-atom is tetra-coordinated. However, in both types of complexes, there is the possibility of penta-coordination in the solid state.

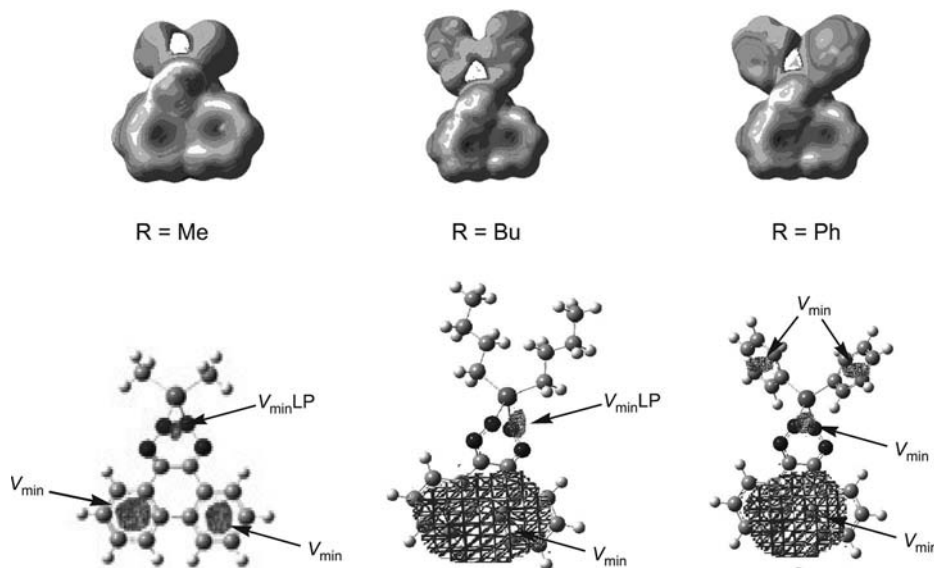
The structures of the complexes were also confirmed by the coupling constants  $^1J(\text{Sn},\text{C})$  and  $^2J(\text{Sn},\text{H})$ , both being directly linked to the C–Sn–C angle ( $\theta$ ) as given in the equations  $^1J(\text{Sn},\text{C}) = 11.4 \theta(\text{C–Sn–C}) - 875$  and  $\theta(\text{C–Sn–C}) = 0.0161[^2J(\text{Sn},\text{H})]^2 - 1.32[^2J(\text{Sn},\text{H})] + 133.4$ . The  $^1J(\text{Sn},\text{C})$  value observed for the dibutyl derivative **2** was 640 Hz, and that for the dimethyl derivative **1** was 590 Hz, these values being in the range of penta-coordinated Sn-atoms [20][21]; the corresponding  $^2J(\text{Sn},\text{H})$  values were 78 and 81 Hz, respectively, consistent with penta-coordinated Sn-atoms [22]. Compounds **4** and **5** had  $^1J$  values of 396.11 and 377.25 Hz and  $^2J$  values of 59 and 57 Hz, respectively, indicating the tetra-coordinated nature of their Sn-atom. Applying the above equations, the C–Sn–C bond angles calculated for the trimethyl and tributyl derivatives **4** and **5** were 111.5 and 109.8, respectively, while for the dimethyl and dibutyl derivatives **1** and **2**, the values were 128.5 and 132.8, respectively.

*Theoretical Calculations.* The ground-state geometry of the ligand 9,10-phenanthrenequinone dioxime was optimized for three types of isomers namely *syn*, *anti*, and *anti-amphi*. The energy values showed that the *anti* (*E,E*) isomer is the most stable. Frequency calculations gave zero imaginary frequency, that is, all were real. Parallel calculations on oxime derivatives were carried out to get more structural information.

For the dialkyl and diphenyl dimeric complexes **1–3**, we first studied the structure of their monomeric units. To obtain information regarding the electron rich centers, the molecular electrostatic potential of the monomer units was analyzed. MESP (molecular electrostatic potential) analysis brings about the effective localization of

electron-rich regions in a molecular system. The minimum points are often located at lone-pair regions and  $\pi$ -bonded regions, and they represent centers of negative charge in the molecule. In the case of the methyl and butyl complexes, the minimum value was found at the O-atoms and the phenanthrene moiety. In the case of the phenyl complex, besides these minimum points, an additional minimum was also observed at the phenyl ligand. The MESP plot for the monomer units of **1–3** is given in *Fig. 2*. In this particular case, regions of attractive potential are shown in dark grey and those of repulsive potential in white. The MESP plot led to the conclusion that the lone-pair strength of the O-atoms was greater than that of the N-atoms. This caused the formation of a coordinate bond between an O-atom of one monomer unit and the Sn-atom of another monomer unit resulting in a dimer.

In the atomic-charge distribution, the Sn-atoms bore a high positive charge and the



*Fig. 2.* Electronic features of the monomer units of **1–3**.  $V_{\min}$  points (considering only the lone-pair region) with isosurface value  $-38.22$ – $32.33$  kcal/mol.

O-atoms a high negative charge. The population analysis also led to the same conclusion that a dimer was formed. *Mulliken* and NPA (natural population analysis) charge distribution at selected atoms of the monomer units of **1–3** are given in *Table 2*.

In performing NBO (natural bond orbitals) analysis of dimers **1–3**, molecules were again treated as two monomer subunits bound through donor–acceptor interactions. NPA Charges at the O-atoms, associated with the Sn–O short and long bonds in dimers, were  $-0.75$  and  $-0.74$ ,  $-0.741$  and  $-0.74$ , and  $-0.742$  and  $-0.745$  for methyl, butyl, and phenyl complexes, respectively. This indicated that relatively little charge was transferred from the O-atoms as compared to the monomer units (*Table 2*). Nonvalent interactions in dimers were analyzed in terms of the second-order-

Table 2. Mulliken and NPA (values in parentheses) Charge Distribution at Selected Atoms of the 1:1 Monomer Units of **1–3**

| Atom    | Monomer unit of      |                      |                      |
|---------|----------------------|----------------------|----------------------|
|         | <b>1</b> (R = Me)    | <b>2</b> (R = Bu)    | <b>3</b> (R = Ph)    |
| C (C=N) | 0.362421 (0.21179)   | 0.363009 (0.21143)   | 0.358787 (0.21036)   |
| C (C=N) | 0.178233 (0.21181)   | 0.361826 (0.21023)   | 0.358793 (0.21036)   |
| N       | –0.277016 (–0.12109) | –0.277953 (–0.12076) | –0.269567 (–0.11515) |
| N       | –0.276971 (–0.12104) | –0.276801 (–0.12045) | –0.269565 (–0.11515) |
| O       | –0.676879 (–0.75812) | –0.673223 (–0.76024) | –0.681803 (–0.76138) |
| O       | –0.676852 (–0.75810) | –0.676707 (–0.76139) | –0.681804 (–0.76138) |
| Sn      | 1.843269 (2.29145)   | 1.840732 (2.31710)   | 2.015735 (2.35388)   |

perturbation theory with the *Fock* matrix constructed in the NBO basis set. Most important nonvalent interactions in dimers **1–3** are presented in *Table 3*. The vacant  $p_z$  orbitals of the metal atoms,  $LP^*Sn$ , interacted with the lone pairs (LPs) of covalently bound O-atoms of the other fragment, leading to  $LP\ O \rightarrow LP^*Sn$ . It is clear from *Table 3* that  $LP\ O^1 \rightarrow LP^*Sn^2$  and  $LP\ O^2 \rightarrow LP^*Sn^1$  were strong interactions in comparison to  $LP\ N^1 \rightarrow LP^*Sn^2$  and  $LP\ N^2 \rightarrow LP^*Sn^1$ . Thus, each Sn-atom formed an ‘intermolecular’ coordination bond with the O-atom of the second subunit.

Table 3. Most Important Nonvalent Interactions in Dimers **1–3** in the NBO Basis. LP = lone pair.

| Compound          | Donor    | Acceptor   | $E(2)$ [kcal/mol] |
|-------------------|----------|------------|-------------------|
| <b>1</b> (R = Me) | LP $O^1$ | $LP^*Sn^2$ | 87.55             |
|                   | LP $N^1$ | $LP^*Sn^2$ | 2.55              |
|                   | LP $O^2$ | $LP^*Sn^1$ | 73.79             |
|                   | LP $N^2$ | $LP^*Sn^1$ | 3.41              |
| <b>2</b> (R = Bu) | LP $O^1$ | $LP^*Sn^2$ | 70.68             |
|                   | LP $N^1$ | $LP^*Sn^2$ | 1.58              |
|                   | LP $O^2$ | $LP^*Sn^1$ | 56.89             |
|                   | LP $N^2$ | $LP^*Sn^1$ | 2.67              |
| <b>3</b> (R = Ph) | LP $O^1$ | $LP^*Sn^2$ | 30.03             |
|                   | LP $N^1$ | $LP^*Sn^2$ | 3.07              |
|                   | LP $O^2$ | $LP^*Sn^1$ | 21.18             |
|                   | LP $N^2$ | $LP^*Sn^1$ | 2.19              |

Compared to the structures of monomer units, the M–O covalent bonds in dimers **1–3** were 0.12 Å longer. The tricoordinated O-atoms from the two monomer units created a four-membered  $Sn_2O_2$  ring. The  $Sn \cdots O'$  coordination bond was the longest one in the dimers (*Table 4*). Due to this coordination, intramonomer Sn–O bonds had unequal lengths. In the central  $Sn_2O_2$  ring, the length of the  $Sn \cdots O'$  bonds were less than the sum of the covalent radii of Sn and O (2.13 Å). Relevant geometrical parameters of the dimers **1–3** are given in *Table 4*.

Frequency calculations were done with the optimized structures of the trialkyl/triphenyl complexes to evaluate the thermodynamic stability of the complexes. The stability constants of the complexes were then derived from the equation  $\Delta G =$

Table 4. Gas-Phase-Optimized Parameters of 1:1 Complexes 1–3

| Compound          | $r(\text{Sn}^1-\text{O}^1)$ | $r(\text{Sn}^1-\text{O}^1)$ | $r(\text{O}^1 \cdots \text{Sn}^2)$ | $\theta(\text{O}^1-\text{Sn}^1-\text{O}^2)$ | $\theta(\text{O}-\text{Sn}^1-\text{O}^1)$ | $\theta(\text{C}-\text{Sn}-\text{C})$ | $\theta(\text{Sn}^1-\text{O}^1-\text{Sn}^2)$ |
|-------------------|-----------------------------|-----------------------------|------------------------------------|---|---|---------------------------------------|--|
| <b>1</b> (R = Me) | 1.980                       | 2.043                       | 2.122                              | 65.89                                       | 80.42                                     | 119.14                                | 110.28                                       |
| <b>2</b> (R = Bu) | 1.979                       | 2.051                       | 2.126                              | 65.74                                       | 80.28                                     | 115.64                                | 111.85                                       |
| <b>3</b> (R = Ph) | 1.972                       | 2.034                       | 2.130                              | 65.68                                       | 77.84                                     | 113.17                                | 113.01                                       |

–  $RT \ln K$ . Theoretical calculations of the tin complexes **4–6** indicated that in all complexes, the central atom existed in a tetrahedral geometry. The data of optimized geometries and thermochemistry at 298.15 K of these complexes are given in Table 5.

Table 5. Gas-Phase-Optimized Parameters and Thermal Data of 1:2 Complexes 4–6 at 298.15 K

| Compound          | $r(\text{Sn}^1-\text{O}^1)$ | $r(\text{Sn}-\text{C})$ | $r(\text{Sn}^2-\text{O}^2)$ | $\theta(\text{C}-\text{Sn}-\text{C})$ | $\Delta E$ [kJ/mol] | $\Delta H$ [kJ/mol] | $\Delta G$ [kJ/mol] | Log $K$ |
|-------------------|-----------------------------|-------------------------|-----------------------------|---------------------------------------|---------------------|---------------------|---------------------|---------|
| <b>4</b> (R = Me) | 2.134                       | 2.174                   | 2.016                       | 112.07                                | – 468.50            | – 464.75            | – 465.95            | 81.62   |
| <b>5</b> (R = Bu) | 2.012                       | 2.164                   | 2.012                       | 109.69                                | – 71.09             | – 64.88             | – 45.75             | 8.01    |
| <b>6</b> (R = Ph) | 2.010                       | 2.075                   | 2.131                       | 112.05                                | – 91.18             | – 73.36             | – 59.27             | 10.38   |

**Conclusions.** – A series of methyl, butyl, and phenyl complexes of the general formula  $[\text{SnR}_2\text{L}]$  and  $[(\text{SnR}_3)_2\text{L}]$  were prepared from the ligand and the corresponding chlorostannane in a 1:1 and 1:2 molar ratio, respectively. The proposed structures of the complexes based on experimental results were also confirmed by computational methods. The thermodynamic stability of the complexes **4–6** were in the order  $[(\text{SnMe}_3)_2\text{L}] > [(\text{SnPh}_3)_2\text{L}] > [(\text{SnBu}_3)_2\text{L}]$ . The NBO analysis clearly revealed the coordination bond between the O-atom of one monomer fragment and the Sn-atom of another monomer fragment in the 1:1 complexes leading to the formation of dimers **1–3**. The Sn-atoms in the 1:1 complexes were penta-coordinated and in the 1:2 complexes tetra-coordinated. The optimized structures of complexes **2** and **5** are given in Fig. 3, and the remaining ones can be obtained as supporting information<sup>1)</sup>.

The financial support of this work by the Department of Atomic Energy/Board of Research in Nuclear Sciences (DAE/BRNS) (2009/37/31/BRNS/2099) is hereby gratefully acknowledged.

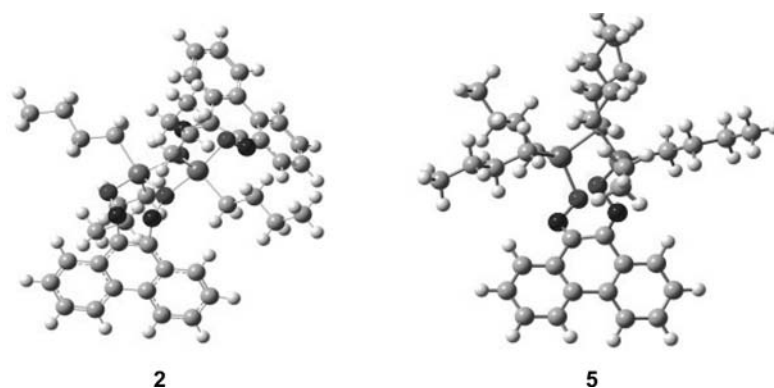
### Experimental Part

*General.* All the chemicals were purchased from Merck and Aldrich and used without further purification. All the reactions were carried out under dry conditions. Solvents were dried by standard methods [23]. M.p.: Perfit apparatus; uncorrected. IR Spectra: Nicolet-Shimadzu spectrometer (range 4000–200  $\text{cm}^{-1}$ ); KBr pellets and  $\text{CCl}_4$  solns.  $^1\text{H}$ -,  $^{13}\text{C}$ -, and  $^{119}\text{Sn}$ -NMR Spectra: Jeol-300AL-FT-NMR spectrometer; at 300, 75.5, and 111.9 Hz, resp.; in  $\text{CDCl}_3$  and  $(\text{D}_6)\text{DMSO}$  ( $^1\text{H}$ - and  $^{13}\text{C}$ ) and in  $\text{C}_6\text{D}_6$  ( $^{119}\text{Sn}$ ), with  $\text{Me}_4\text{Si}$  as internal standard and  $\text{Me}_4\text{Sn}$  as external standard, resp. Elemental analyses: estimation of the Sn-content as tin oxide, and of the N-content as reported in [24].

*Computational Details.* The gas-phase calculations of the structural and electronic properties of the metal complexes and the ligand were performed with the Gaussian 03 suite of programs [25]. Restricted

<sup>1)</sup> Electronic supplementary material is available from the corresponding author P. Pardasani.



Fig. 3. *Optimized geometries of complexes 2 and 5*

density-functional calculations were carried out by means of this package, with the B3LYP hybrid method that employs the *Becke* three parameters exchange functional and the *Lee–Yang–Parr* correlation functional. This functional has been established to be effective for the determination of the optimal geometries, harmonic frequencies, and electronic properties of complexes. Considering the size of the dimeric complexes and our calculation tools, HF/3-21G was also used for calculation of the 1 : 1 complexes.

*Phenanthrene-9,10-dione 9,10-Dioxime* ( $H_2L$ ). Ligand  $H_2L$  was prepared by the reaction of phenanthrene-9,10-dione (0.8328 g, 4 mmol) and hydroxylamine hydrochloride (1.042 g, 15 mmol) in EtOH (25 ml) with sodium acetate (0.8203 g, 10 mmol) and reflux for 12 h (red  $\rightarrow$  yellow during refluxing). Then, the mixture was filtered and the filtrate concentrated to half the volume and kept overnight at r.t. yielding shining yellowish green crystals which were collected and dried under vacuum:  $H_2L$  (83%). M.p. 197–202° ([26]: m.p. 202°).

*Phenanthrene-9,10-dione 9,10-Dioxime Sodium Salt* (1 : 2) ( $Na_2L$ ). To the freshly prepared MeOH soln. (5 ml) of MeONa (0.1728 g, 3 mmol), a soln. of  $H_2L$  (0.3573 g, 1.5 mmol) in benzene (15 ml) was added dropwise (yellowish green  $\rightarrow$  dark brown during the addition). Subsequently, the mixture was refluxed for 5 h.

*Bis*{ $\mu$ -{[phenanthrene-9,10-dione 9,10-Di(oximato- $\kappa O, \kappa O'$ )](2-)}}}tetraphenylditin (**3**). To the MeOH/benzene soln. (10 ml) of  $Na_2L$  (0.2095 g, 0.8 mmol), the benzene soln. of dichlorodiphenylstannane (0.2751 g, 0.8 mmol) was added slowly dropwise at r.t. under  $N_2$  (dark brown  $\rightarrow$  light yellow). The mixture was then refluxed for 5 h to ensure completion of the reaction. The precipitated NaCl was filtered off, the filtrate concentrated, and the light yellow residue washed with hexane and dried under vacuum: **3** (0.3418 g, 42%). Data: Table 6.

Table 6. *Physical and Analytical Data of Organotin(IV) Complexes*

| Compound | Physical appearance   | Yield [%] | M.p. [°C]  | Elemental analysis: found (calc.) [%] |             |             |               |
|----------|-----------------------|-----------|------------|---------------------------------------|-------------|-------------|---------------|
|          |                       |           |            | C                                     | H           | N           | Sn            |
| <b>1</b> | brown solid           | 60        | 203 (dec.) | 51.54 (51.92)                         | 3.80 (3.78) | 5.46 (5.82) | 30.87 (30.46) |
| <b>2</b> | red solid             | 75        | 176        | 57.66 (57.88)                         | 5.70 (5.33) | 4.48 (4.81) | 25.33 (25.38) |
| <b>3</b> | yellow solid          | 42        | 280 (dec.) | 62.57 (62.51)                         | 3.67 (3.33) | 4.13 (4.16) | 23.34 (23.76) |
| <b>4</b> | greenish yellow solid | 68        | 195 (dec.) | 42.60 (41.52)                         | 4.65 (4.10) | 4.97 (4.92) | 42.11 (42.18) |
| <b>5</b> | red solid             | 60        | 104        | 55.91 (55.27)                         | 7.66 (7.18) | 3.43 (3.56) | 29.08 (29.19) |
| <b>6</b> | brown solid           | 50        | 235 (dec.) | 64.14 (63.98)                         | 4.09 (3.54) | 2.99 (2.80) | 25.36 (25.22) |

*Tetrabutylbis*{ $\mu$ -{[phenanthrene-9,10-dione 9,10-Di(oximato- $\kappa$ O, $\kappa$ O': $\kappa$ O')](2-)}*}}*ditin (**2**). As described for **3**. Data: Table 6.

*Tetramethylbis*{ $\mu$ -{[phenanthrene-9,10-dione 9,10-Di(oximato- $\kappa$ O, $\kappa$ O': $\kappa$ O')](2-)}*}}*diitin (**1**). Dichlorodimethylstannane was added to Na<sub>2</sub>L at r.t. under stirring within 5 h. Workup as described for **3**: light brown crystalline **1** (60%). Data: Table 6.

*Hexamethyl*{ $\mu$ -{[phenanthrene-9,10-dione 9,10-Di(oximato- $\kappa$ O: $\kappa$ O')](2-)}*}}*ditin (**4**), *Hexabutyl*{ $\mu$ -{[phenanthrene-9,10-dione 9,10-Di(oximato- $\kappa$ O: $\kappa$ O')](2-)}*}}*diitin (**5**), and  $\mu$ -{[Phenanthrene-9,10-dione 9,10-Di(oximato- $\kappa$ O: $\kappa$ O')](2-)}*}}*hexaphenylditin (**6**). As described for **3**, with Na<sub>2</sub>L and the chloroorganostannane SnR<sub>3</sub>Cl (R = Me, Bu, and Ph) in a 1:2 molar ratio. Data: Table 6.

## REFERENCES

- [1] S. Anderson, *J. Chem. Soc.* **1934**, 971.
- [2] A. G. Beirakhov, I. M. Orlova, Y. N. Mikhailov, R. N. Shchelokov, *Dokl. Chem.* **2001**, 38, 305.
- [3] A. Chakravorty, *Coord. Chem. Rev.* **1974**, 13, 1.
- [4] J. R. Dilworth, S. J. Parrot, *Chem. Soc. Rev.* **1998**, 27, 43.
- [5] S. J. Blunden, P. A. Cusack, R. Hill, 'The Industrial Uses of Tin Chemicals', Whitstable Litho, UK, 1985.
- [6] G. K. Sandhu, R. Gupta, S. S. Sandhu, R. V. Parish, *Polyhedron* **1985**, 4, 81.
- [7] J. C. Cochran, H. K. Philips, S. Tom, A. R. Hund, B. S. Bronk, *Organometallics* **1994**, 13, 947.
- [8] M. Mohammad, S. Khadija, M. Sohail, A. Saqib, B. Moazzam, *Turk. J. Chem.* **2004**, 28, 17.
- [9] H. Jason, C. Kieran, R. Pratt, *Biochem. Biophys. Res. Commun.* **2000**, 274, 732.
- [10] Y. T. Zhou, S. Ren, J. Yu, Z. Xia, *J. Organomet. Chem.* **2005**, 69, 2186.
- [11] P. Pardasani, D. Kumar, *Main Group Met. Chem.* **2004**, 27, 233.
- [12] P. Pardasani, I. Sharma, D. Kumar, *J. Indian Chem. Soc.* **2004**, 81, 230.
- [13] C. E. Holloway, M. Melnik, *Main Group Met. Chem.* **2000**, 23, 331.
- [14] C. E. Holloway, M. Melnik, *Main Group Met. Chem.* **2001**, 24, 467.
- [15] M. Sharma, P. Pardasani, *Main Group Met. Chem.* **2008**, 31, 227.
- [16] H. L. Singh, A. K. Varshney, *Appl. Organomet. Chem.* **2001**, 15, 762.
- [17] M. Danish, H. G. Alt, A. Badsha, S. Ali, M. Mazhar, *J. Organomet. Chem.* **1995**, 486, 51.
- [18] L. Angiolini, D. Caretti, E. Cavicchi, *Anno Accad.* **2009**, 4, 17.
- [19] J. Otera, *J. Organomet. Chem.* **1981**, 221, 57.
- [20] T. B. Grindley, R. Thangarasa *J. Am. Chem. Soc.* **1990**, 112, 1364.
- [21] T. P. Lockhart, W. F. Manders, J. J. Zuckerman, *J. Am. Chem. Soc.* **1985**, 107, 4546.
- [22] A. K. Gupta, S. Sharma, H. P. S. Chauhan, R. J. Rao, *Synth. React. Inorg. Met.-Org. Chem.* **1991**, 21, 497.
- [23] W. L. F. Armarego, D. D. Perrin, 'Purification of Laboratory Chemicals', 4th edn., Butterworth, Oxford, 1997.
- [24] A. I. Vogel, 'Textbook of Quantitative Chemical Analysis', 4th edn., Longman, London, 1989.
- [25] Gaussian 03 Revisions D.O.I., M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian 98, Revision A.5, Gaussian, Inc., Pittsburgh, 1998.
- [26] J. H. Boyer, R. F. Reinisch, M. J. Danzig, G. A. Stoner, F. Sahhar, *J. Am. Chem. Soc.* **1955**, 77, 5688.

Received May 15, 2012