

Synthesis and structure peculiarities of tin (IV) complexes with tetradentate redox-active ligand

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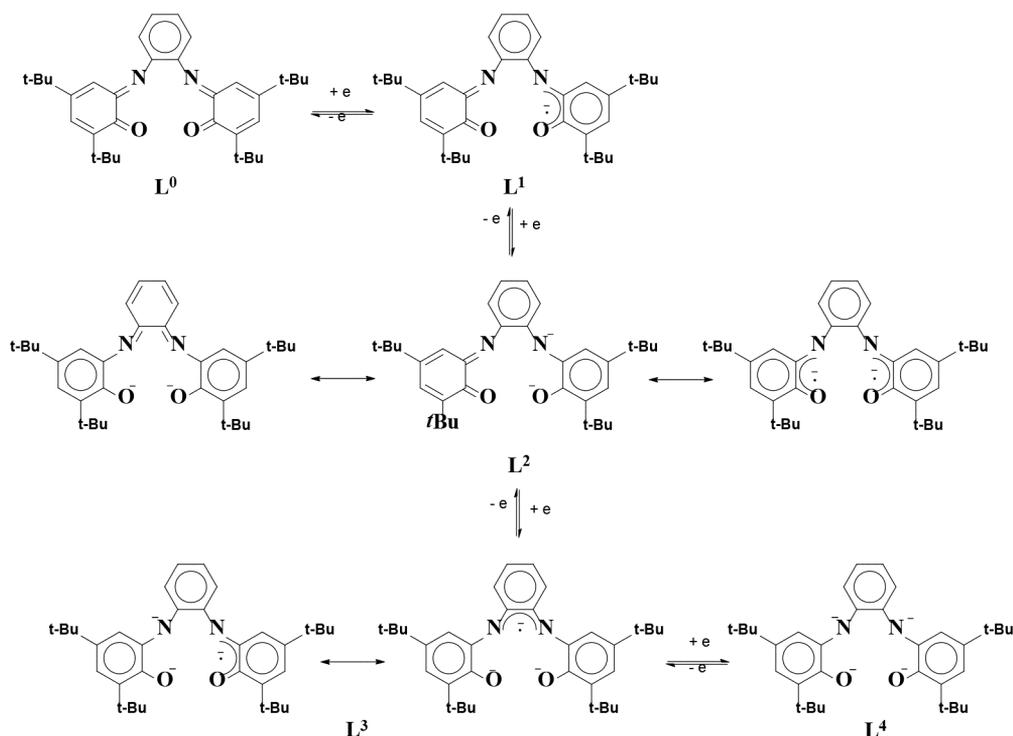
Tin(IV) complexes containing an organic ligand, the dianion of the redox-active N, N'-bis-(3,5-di-tert-butyl-2-hydroxyphenyl)-1,2-phenylenediamine, have been synthesized. The crystal and molecular structure was investigated by the method of X-ray analysis. It has been established that for the obtained compounds, the main singlet and thermally populated triplet spin states are realized.

Keywords: tin (IV), dianion ligand, crystal structure, molecular structure, thermally populated triplet spin state.

1. Introduction

The study of compounds of metals with organic redox-active ligands has been one of the priorities areas in coordination and organometallic chemistry over the past few decades. The introduction of ligands of this type into the composition of organometallic compounds allows, in some cases, to significantly affect their reactivity [1]. *N,N'*-bis-

(3,5-di-*tert*-butyl-2-hydroxyphenyl)-1,2-phenylenediamine (H_2L^4) [2] is a promising ligand for the synthesis of stable derivatives of metals, due to the creation of larger spatial shielding in close proximity to the central metal atom. This ligand is able to exist in five different redox states, being bound to a complex with a metal which significantly increases the variety of possible electronic structures, and al-



Scheme 1.

so allows fine-tuning the redox properties of compounds derived from it. The mono- (L^1) and trianionic (L^3) forms of the ligand are paramagnetic, and the di- (L^2), tetraanion (L^4) and the neutral form (L^0) are diamagnetic. But the dianionic form of the ligand can exist in both the singlet and triplet states (Scheme 1).

The main method for the synthesis of metal complexes based on this ligand is the direct interaction of N, N'-bis(2-hydroxy-3,5-di-tert-butylphenyl)-1,2-phenylenediamine with metal salts under various conditions [2-7]. The first examples of such compounds were zinc and copper derivatives [2]. The authors [3-6] developed approaches to the synthesis of compounds of metals Ti, Zr, Hf and Mo, containing a ligand in tetraanionic (L^4) [3,4], dianionic (L^2) [3,4,6] and dianionic, twice protonated (H_2L^2) [5] forms. Interestingly, depending on the ratio of metal salt : ligand, different products are formed. For example, mononuclear and binuclear derivatives of titanium and zirconium, which exhibit catalytic activity in the polymerization of lactides, were obtained in [5]. At the moment, two complexes are known that contain two such tetradentate ligands. They are an octa-coordinated complex of tin, the composition of L^2_2Sn [7] and the heptacoordinated complex of molybdenum, in which one ligand is in the dianionic (L^2) and the second in the dianionic monoprotonated (HL^2) forms [6].

In this work, organometallic compounds Me_2SnL^2 (**1**) and Ph_2SnL^2 (**2**), containing tetraden-

tate redox-active N,N'-bis(2-hydroxy-3,5-di-tert-butylphenyl)-1,2-phenylenediamine in dianionic form, were first synthesized and characterized.

2. Results and Discussion

Tin complexes **1** and **2** containing tetradentate redox-active ligand in the dianionic state were obtained by the reaction of N,N'-bis-(3,5-di-tert-butyl-2-hydroxyphenyl)-1,2-phenylenediamine [2] with diorganodihalogenides of tin in methanol (Scheme 2). The synthesis was carried out in two successive stages. In the first of these, tin complexes with the preservation of N – H bonds in the ligand were obtained, from the exchange reaction in the absence of oxygen. Next, the resulting derivatives are oxidized with a dosed amount of air oxygen for 24 hours. Tin complexes **1** and **2** are isolated from the reaction mixtures in the form of dark green crystalline products. The compounds obtained in the crystalline state are resistant to the action of oxygen and moisture in the air. Figure 1 shows the molecular structure of compound **1**. The crystals of the complex, suitable for X-ray diffraction, were obtained by slow evaporation of the reaction mixture.

It should be noted that an excess of oxygen at the second stage of the reaction does not lead to the obtaining of desired compounds. Thus, carrying out the second stage of the reaction under conditions of free access of air oxygen is accompanied by the appearance of an intense brown dyeing of the reaction mixture, from which colorless crystals

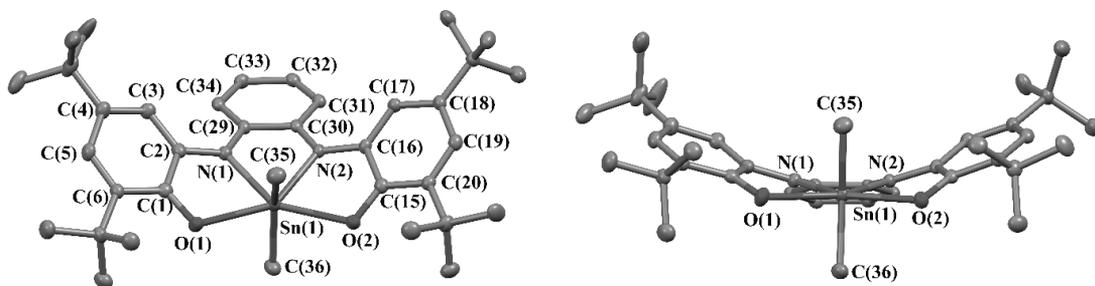
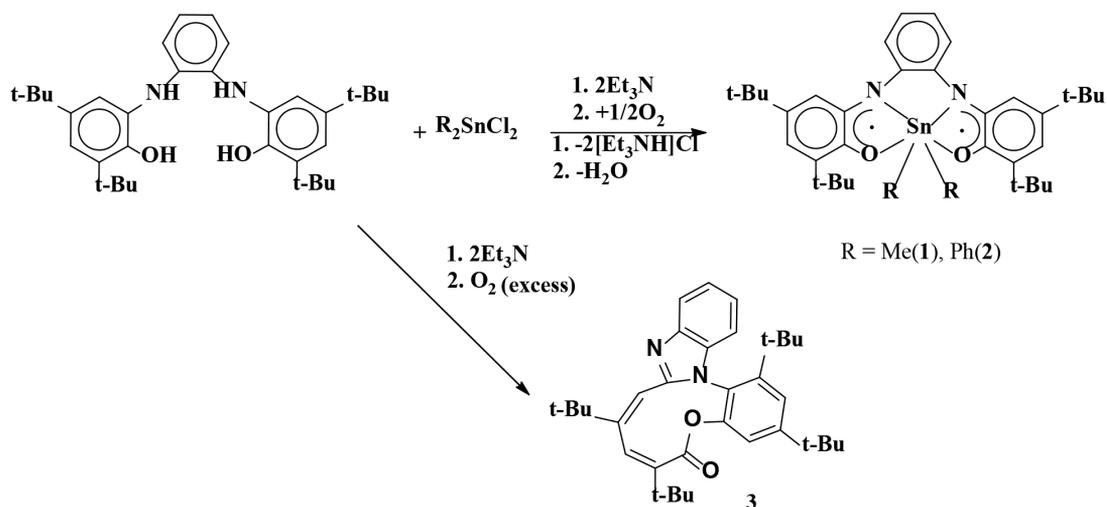


Figure 1. Views of molecular structure of complex **1**. Hydrogen atoms are not shown. Thermal ellipsoids of 50% probability are given. Basic bond lengths (Å) are: Sn(1)-O(1) 2.279(2), Sn(1)-O(2) 2.298(2), Sn(1)-N(1) 2.222(3), Sn(1)-N(2) 2.227(2), Sn(1)-C(36) 2.104(3), Sn(1)-C(35) 2.115(3), O(1)-C(1) 1.292(4), O(2)-C(15) 1.289(3), N(1)-C(29) 1.351(4), N(1)-C(2) 1.369(3), N(2)-C(30) 1.341(4), N(2)-C(16) 1.375(3), C(1)-C(6) 1.440(4), C(1)-C(2) 1.441(4), C(2)-C(3) 1.410(4), C(3)-C(4) 1.383(4), C(4)-C(5) 1.430(4), C(5)-C(6) 1.365(4), C(29)-C(34) 1.422(4), C(29)-C(30) 1.453(4), C(30)-C(31) 1.426(4), C(31)-C(32) 1.361(4), C(32)-C(33) 1.411(4), C(33)-C(34) 1.360(4), C(15)-C(16) 1.442(4), C(15)-C(20) 1.442(4), C(16)-C(17) 1.415(4), C(17)-C(18) 1.371(4), C(18)-C(19) 1.424(4), C(19)-C(20) 1.370(4). Selected Valence Angles (°): C(36)-Sn(1)-C(35) 148.75(13), C(36)-Sn(1)-N(1) 104.28(12), C(35)-Sn(1)-N(1) 101.63(11), C(36)-Sn(1)-N(2) 104.12(11), C(35)-Sn(1)-N(2) 100.27(11), N(1)-Sn(1)-N(2) 72.00(8), C(36)-Sn(1)-O(1) 86.55(11), C(35)-Sn(1)-O(1) 85.41(10), N(1)-Sn(1)-O(1) 71.42(8), N(2)-Sn(1)-O(1) 143.38(8), C(36)-Sn(1)-O(2) 85.57(11), C(35)-Sn(1)-O(2) 84.12(11), N(1)-Sn(1)-O(2) 143.09(8), N(2)-Sn(1)-O(2) 71.10(8), O(1)-Sn(1)-O(2) 145.40(7).



Scheme 2.

of 1,3,7,9-tetra-tert-butyl-6H-benzo [b]benzo[4,5]imidazo[1,2-d][1,4]oxazecin-6-on (**3**) (is a product of degradation of the original organic ligand) were obtained (Scheme 2). The structure of compound **3** was established by X-ray diffraction (Figure 2). The distribution of bond lengths and angles in molecule **3** uniquely corresponds to the proposed formula.

The crystal cell of compound **1** contains three crystallographically independent molecules of the complex. In general, the geometries of these molecules are close to each other, and in the future we will consider one of them. The coordination sphere of the tin atom in complex **1** is a distorted octahedron formed by two methyl substituents in the apical positions and a tetradentate chelating ligand forming the equatorial plane. The ligand in compound **1** has a bath conformation, which significantly distinguishes it from its closest analogues — the hexacoordinated compound Cl_2TiL^2 [4] and organometallic compounds of tin(IV) and lead(IV) containing a similar almost planar dianion tetradentate ligand [8]. The dihedral angle between the O(1)-C(1)-C(6)-N(1) and O(2)-C(15)-C(20)-N(2) planes in compound **1** is 42.14° . An analysis of the bond lengths in compound **1** shows that the tetradentate organic fragment is the biradical form of the L^2 ligand. Thus, the quinoid alternation of C-C bonds in C(1)-C(6) and C(15)-C(20) rings, as well as C(1)-O(1), C(2)-N(1), C(15)-O(2) and C(16)-N(2) are in the range characteristic of the known *o*-iminosemiquinone derivatives of tin(IV) [9-11]. The processing of structural study data in the framework of the model proposed in [12] allows calculating the formal oxidation state of ON-chelating fragments, each of which is -0.98 ± 0.11 ,

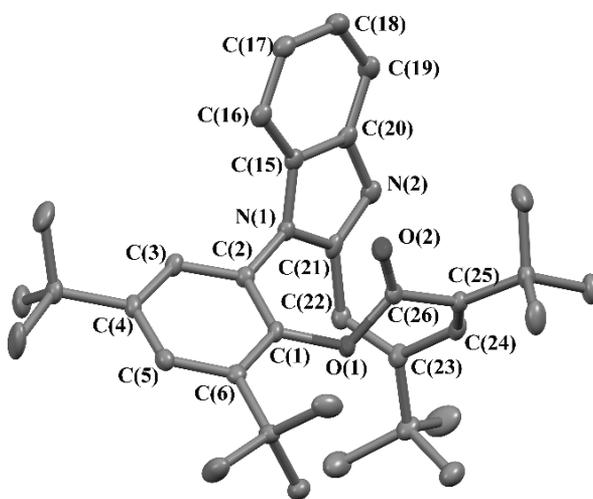


Figure 2. Views of molecular structure of compound **3**. Hydrogen atoms are not shown. Thermal ellipsoids of 30% probability are given. Basic bond lengths (Å) are: (Å): O(1)-C(26) 1.3762(14), O(1)-C(1) 1.4103(16), O(2)-C(26) 1.1961(17), N(1)-C(21) 1.3846(18), N(1)-C(15) 1.3881(15), N(1)-C(2) 1.4299(14), N(2)-C(21) 1.3167(13), N(2)-C(20) 1.3917(18), C(1)-C(6) 1.3882(16), C(1)-C(2) 1.3992(17), C(2)-C(3) 1.381(2), C(3)-C(4) 1.3825(16), C(4)-C(5) 1.3857(18), C(5)-C(6) 1.400(2), C(15)-C(16) 1.388(2), C(15)-C(20) 1.4061(18), C(16)-C(17) 1.3843(16), C(17)-C(18) 1.402(2), C(18)-C(19) 1.374(2), C(19)-C(20) 1.3913(16), C(21)-C(22) 1.4607(18), C(22)-C(23) 1.338(2), C(23)-C(24) 1.481(2), C(24)-C(25) 1.332(2).

which also clearly indicates the radical-anion nature of iminoquinone cycles.

The ^1H NMR spectrum of compounds **1** and **2**, registered in CDCl_3 , contains narrow peaks from the protons of the tert-butyl groups that make up the ligand and from the protons belonging to the hydrocarbon substituents at the metal atom. At the same time, a significant broadening of the lines is observed in the aromatic region of the spectrum. This fact indicates a possible paramagnetic component in the samples under study. It should be noted that due to the presence of the paramagnetic component in the sample in the CDCl_3 solution, it is impossible to register the ^{13}C and ^{119}Sn NMR spectra. Lowering the temperature from $+50$ to -50 °C leads to a narrowing of the lines in the aromatic region of the ^1H NMR spectrum (Fig. 3). This behavior, in combination with the X-ray diffraction analysis, indicates that biradical compounds **1** and **2** have the main singlet spin state and the thermally populated triplet state, which is occupied with increasing temperature. This statement is also confirmed by the data of magnetochemical measurements. At room temperature, the effective magnetic moment values are 1 and 0.5 μB for crystalline samples of complexes **1** and **2**, respectively. Lowering the temperature leads to a decrease in the values of the effective magnetic moment almost to zero at a temperature of 4 K.

It should be noted that the broadening of lines in the aromatic region of the spectrum is observed not only for tin complexes **1** and **2**. Analogous broadening in the proton NMR spectrum is described for the zirconium complex containing the tetradentate ligand in the dianionic state [3]. From the analysis of the XRD data of the compound, it follows that the ONNO-ligand is not planar, but has the shape of a bath, like tin complexes. The value of the dihedral angle between the phenol fragments of the ligand in the heptacoordinated $\text{Zr}(\text{L}^2)\text{Cl}_2 \cdot \text{THF}$ compound is 29.4° . At the same time, in the titanium complex $\text{Ti}(\text{L}^2)\text{Cl}_2$ [3], according to X-ray diffraction data, the ligand is almost planar, and in the proton NMR spectrum, no broadening of the lines in the aromatic region is observed. From the listed facts, it can be concluded that the ligand conformation in the coordination sphere of a metal determines the possibility of realizing a triplet state for it.

According to the X-ray diffraction study of complex **1**, the tin atom has a vacant space between two hydrocarbon substituents, sufficient to coordinate the additional ligand on the metal, which occurs in the solution of coordinating solvents. Such coordination leads to an increase in the coordination number of the metal from six to seven and the angle between the hydrocarbon substituents, which is vividly demonstrated by NMR spectroscopy data. The constant of spin-spin interaction of protons of a hydrocarbon group with magnetic tin isotopes

($^1J(^{119}\text{Sn}, ^1\text{H})$) linearly depends on the angle between these substituents at the metal atom — an increase in the angle leads to an increase in the corresponding constant [13]. When the CDCl_3 solvent is replaced by a donor deuteropyridine, the spin-spin interaction constant ($^1J(^{119}\text{Sn}, ^1\text{H})$) in complex **1** increases from 96.4 to 109.6 Hz. This indicates an increase in the Me-Sn-Me angle caused by the coordination of the pyridine molecule to the metal atom.

It should be noted that a change in the coordination environment of the tin atom during the coordination of the pyridine molecule on the metal in complex **1** contributes to the stabilization of the sin-

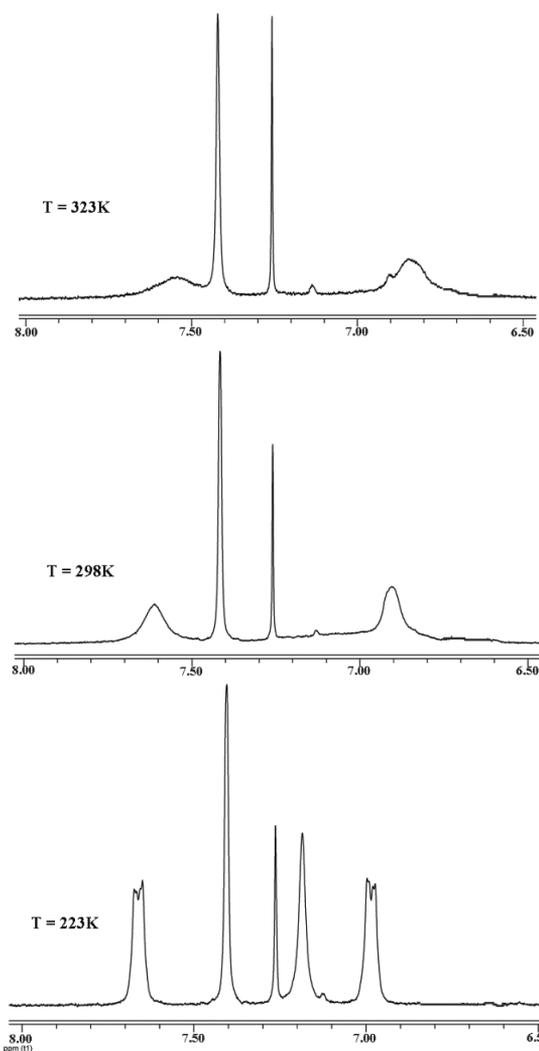


Figure 3. The aromatic region of the ^1H NMR spectrum of complex **1** at various temperatures in CDCl_3 .

glet state of the dianionic tetradentate ligand in the resulting compound. When complex **1** is dissolved in deuteropyridine, the broadening of lines in the aromatic region of the spectrum is absent even at room temperature and a well resolved not only proton NMR spectrum, but also spectra on ^{13}C and ^{119}Sn nuclei are recorded. Probably, coordination of the pyridine molecule to tin results in the elongation of the metal ion from the chelate cycle of the tetradentate ligand, which leads to a change in the conformation of the latter. This, in turn, stabilizes the ground singlet spin state and makes the triplet state unattainable. Coordination of donor solvent molecules by complexes **1** and **2** is also accompanied by a solvatochromic change in their electronic absorption spectra. The spectrum for **1** or **2** in the range of 300–1500 nm contains three intense bands due to electronic ILCT transitions. According to the data of electronic absorption spectroscopy of complex **1**, the absorption bands are shifted to a shorter wavelength region of the spectrum in donor solvents. The largest shift (> 100 nm) is observed for transitions in the near-IR spectral region (Fig. 4). This observation also indicates a significant change in the energy of the frontier orbitals of the complex, which are predominantly ligand in nature. Earlier, tin(IV) complexes based on another redox-active tetradentate ligand showed similar behavior [8].

3. Experiment

NMR spectra were obtained in d_5 -Py and CDCl_3 using a Bruker Avance III NMR spectrometer (400 MHz) with the internal standard Me_4Si . The electron absorption spectra were recorded on a UV-VIS-NIR Spektrophotometer SHIMADZU UV-3600 spectrometer. IR spectra were recorded on an FSM-1201 Fourier transform infrared spectrometer (suspensions in liquid paraffin; KBr cells).

We used commercial reagents: Me_2SnCl_2 and Ph_2SnCl_2 . *N,N'*-bis-(3,5-di-*tert*-butyl-2-hydroxyphenyl)-1,2-phenylenediamine (LH_4) was synthesized according to a known procedure [2]. The solvents used in the work were purified and dried as recommended [14].

Synthesis of complexes 1 and 2.

N,N'-bis-(3,5-di-*tert*-butyl-2-hydroxyphenyl)-1,2-phenylenediamine (LH_4) (0.516 g, 1 mmol) and Me_2SnCl_2 (0.22 g, 1 mmol) (or tin dichlorodiphenyltin(IV) (0.34 g, 1 mmol)) in 30 ml of acetonitrile in the presence of triethylamine (0.3 ml). The reaction mixture was stirred for 30 minutes after which 60 ml of atmospheric air was filled into the ampoule, which led to the gradual appearance of intense green staining. The resulting solution was kept for 24 hours at room temperature, which was accompanied by the precipitation of a crystalline green precipitate of compounds **1** (**2**). The precipitate was collected on a Schott filter.

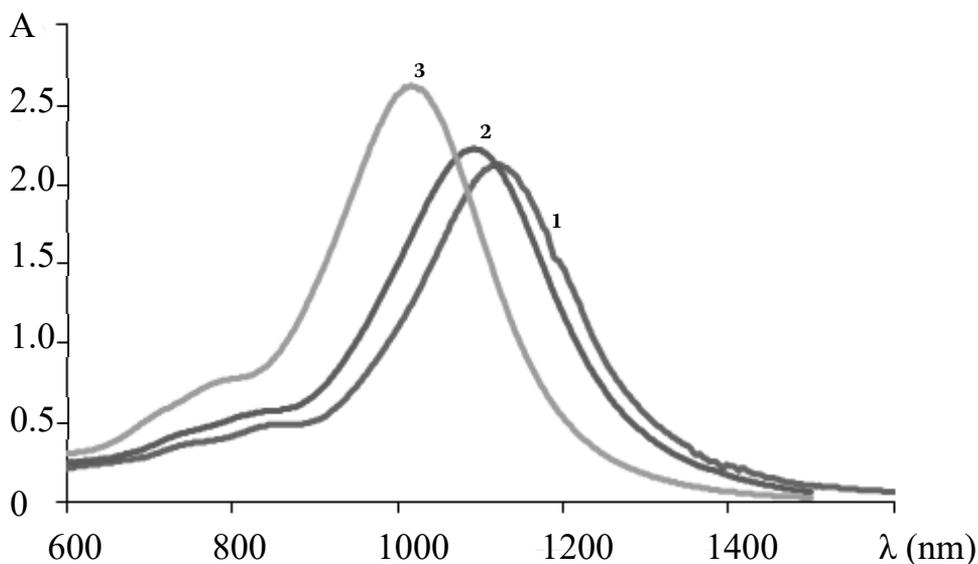


Figure 4. The near IR region of the electronic absorption spectrum of complex **1** in various solvents ($C = 1 \times 10^{-4}$ M, $l = 1$ cm): 1) Toluene; 2) Tetrahydrofuran; 3) Pyridine.

Crystals **1** suitable for XRD were obtained by slow crystallization of the complex from acetonitrile

It is obtained: 0.46 g (0.69 mmol) of complex **1**. Specific yield is 70%.

It is found (%): C, 65.64; H, 7.84. Calculated (%): C, 65.36; H, 7.62 for $C_{36}H_{50}SnN_2O_2$.

IR spectrum, ν (cm^{-1}): 1518 s., 1400 m., 1363 s., 1300 m., 1272 s., 1197 s., 1167 s., 1127 s., 1113 s., 1025 m., 911 s., 870 m., 749 s., 731 s., 634 m., 587 m., 568 m., 505 s.

Electronic absorption spectrum: $\lambda(\epsilon, l \cdot cm^{-1} \cdot mol^{-1})$: toluene 369 (15100), 471 (2700), 1122 (21800); tetrahydrofuran 363(14439), 466(2754), 1092(22262); pyridine 340 (15274), 460 (2943), 1017 (26215).

1H NMR (400 MHz, $CDCl_3$, 223 K, $\delta/ppm, J/Hz$): 0.45 (c., 6 H, $J(^{119}Sn-^1H) = 96.4$, Sn- CH_3), 1.28 (c., 18 H, t-Bu), 1.38 (c., 18 H, t-Bu), 6.98 (sign. br., 2 H, H_{arom}), 7.18 (c., 2 H, H_{arom}), 7.40 (c., 2 H, H_{arom}), 7.66 (sign. br., 2 H, H_{arom}).

1H NMR (400 MHz, d_5 -Py, 293 K, $\delta/ppm, J/Tu$): 0.58 (c., 6 H, $J(^{119}Sn-^1H) = 109.6$, Sn- CH_3), 1.30, (c., 18 H, t-Bu), 1.44 (c., 18 H, t-Bu), 6.90 (sign. br., 2 H, H_{arom}), 7.51 (sign. br., 2 H, H_{arom}), 7.60 (ysh. sig., 4 H, H_{arom}).

^{13}C NMR (100 MHz, d_5 -Py, 293 K, δ/ppm): 11.6 (Sn- CH_3), 29.41, 31.11 (CH_3 (t-Bu)), 34.46, 35.35 (C(t-Bu)), 15.53, 115.87, 117.16, 118.93, 127.04, 129.16, 135.99, 139.60, 140.67, 145.54 (C_{apom}), 165.91 (C=N).

^{119}Sn NMR (149 MHz, d_5 -Py, 293 K, δ/ppm): -358.99.

Obtained: 0.60 g (0.76 mmol) of complex **2**. Specific yield is 76%.

It is found (%): C, 70.54; H, 7.07. Calculated (%): C, 70.32; H, 6.93 for $C_{46}H_{54}SnN_2O_2$. IR spectrum, ν (cm^{-1}): 1519 s., 1397 m., 1368 s., 1290 m., 1256 s., 1197 m., 1165 s., 1128 s., 1117 s., 1061 m., 1025 m., 913 s., 847 m., 748 s., 732 s., 695 m., 633 m., 591 m., 585 m., 503 s.

Electronic absorption spectrum, toluene $\lambda(\epsilon, l \cdot cm^{-1} \cdot mol^{-1})$: 364 (12513), 473 (2540), 1131 (17483).

1H NMR (400 MHz, $CDCl_3$, 273 K, $\delta/ppm, J/Hz$): 1.34 (c., 18 H, t-Bu), 1.35 (c., 18 H, t-Bu), 6.84 (sign. br., 2 H, H_{arom}), 7.12 (m., 8 H, H_{arom}), 6 H(Ph-Sn), 7.44 (c., 2 H, H), 7.49 (m., 2 H, H(Ph-Sn)), 7.60 (sign.br., 2 H, H_{arom}).

XRD of compounds **1** and **3** was carried out on a Smart Apex diffractometer (MoK_α , graphite monochromator, $\omega - \phi$ scanning). The structure of the compounds is deciphered by direct methods and refined on the OLS by F^2 in the full-matrix anisotropic approximation for all non-hydrogen atoms (SHELXTL) [38]. Absorption is accounted for by the SADABS program [39].

For crystal **1** 99778 reflections were measured, of which 23895 ($R_{int} = 0.0610$) are independent with $I > 2\sigma(I)$. The crystals **1** are monoclinic, with 100(2) K: $a = 29.7852(8)$, $b = 21.4767(6)$, $c = 16.4411(5)$ Å,

$\alpha = 90^\circ$, $\beta = 97.9200(10)^\circ$, $\gamma = 90^\circ$; sp. gr. P2(1)/c, Z = 12, $V = 10416.9(5)$ Å³, $\rho(\text{calc.}) = 1.265$ g/cm³, $\mu = 0.767$ mm⁻¹, $1.17 \leq \theta \leq 27.00^\circ$, $R1 = 0.0431$, $wR2 = 0.0768$ ($I > 2\sigma(I)$), $R1 = 0.0907$, $wR2 = 0.851$ (according to all data), $S(F2) = 1.010$.

For crystal **3** 17576 reflections were measured, of which 5971 ($R_{int} = 0.0605$) are independent with $I > 2\sigma(I)$. The crystals **3** are monoclinic, with 100(2) K: $a = 30.1927(18)$, $b = 9.8443(6)$, $c = 25.2931(15)$ Å, $\alpha = 90^\circ$, $\beta = 125.8220(10)^\circ$, $\gamma = 90^\circ$; sp. gr. C2/c, Z = 8, $V = 6095.7(6)$ Å³, $\rho(\text{calc.}) = 1.117$ g/cm³, $\mu = 0.069$ mm⁻¹, $1.99^\circ \leq \theta \leq 26.00^\circ$, $R1 = 0.0553$, $wR2 = 0.1114$ ($I > 2\sigma(I)$), $R1 = 0.1121$, $wR2 = 0.1249$ (according to all data), $S(F2) = 1.020$.

Crystallographic data of complexes **1** and **3** are deposited in the Cambridge structural data bank (No 1866478 and 1866477 respectively); deposit@ccdc.cam.ac.uk; (www: http://www.ccdc.cam.ac.uk).

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