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3,6-Di-*tert*-Butyl-2-Hydroxy-4-Pyridinylphenolate and Tin(IV) Complexes It Forms: Synthesis and Structure Details and Solvatochromic Effect

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Abstract—Two synthetic approaches were developed for the preparation of 3,6-di-*tert*-butyl-2-hydroxy-4-pyridinylphenolate (LH), a new zwitter-ionic redox-active diolate type ligand. Two heteroligand five-coordinate tin(IV) derivatives were prepared with this ligand: 3,6-di-*tert*-butyl-2-oxy-4-pyridinylphenolato(triphenyl)tin(IV) (**I**) and 3,6-di-*tert*-butyl-2-oxy-4-pyridinylphenolato(diphenyl)chlorotin(IV) (**II**). The molecular structures of the ligand LH · 0.5Py and complex **I** · CH_3CN were determined by X-ray diffraction (CIF files CCDC nos. 1974166 (LH), 1974165 (**I**)). It was shown that the ligand LH and the tin(IV) compound exhibit solvatochromism, which consists in a considerable blue shift with increasing solvent polarity.

Keywords: diolate ligand, zwitter-ion, tin(IV), X-ray diffraction, ESR spectroscopy, electronic absorption spectroscopy, solvatochromism

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INTRODUCTION

o-Benzoquinone type compounds are of considerable interest for organoelement and coordination chemistry [1], as they are redox-active ligands that can occur in the metal coordination sphere in three oxidation states: dianion (catecholate), radical anion (semiquinone), and neutral states. Organic ligands of this type are of particular interest for the preparation of main group metal compounds, as they markedly expand the redox properties of derivatives of main group elements [2, 3].

The metal complexes containing ligands of this type in the paramagnetic state are of obvious interest from the standpoint of both intra- and intermolecular magnetic exchange interactions [4]. In addition, the unique ability of benzoquinone derivatives, as redox-active compounds in a metal coordination environment, to undergo reversible interconversions between oxidation states makes it possible to observe the phenomenon of valence tautomerism [5] and to design the electronic structure of metal compounds via redox transformations [6]. The redox reactions of redox-active ligands linked to the complexing ion find use in a number of stoichiometric and catalytic reactions that are not accompanied by a change in the oxidation state of the central ion [7–11]. Notably, most of the known coordination compounds with ligand systems of this type are formed by singly and doubly reduced redox forms, whereas the range of metal complexes based on neutral ligands [12] is scarce. There are also only few metal benzoquinone derivatives with a mixed coordination mode in which the redox-active ligand is bound to the complexing ion by both covalent and donor-acceptor bonds [13, 14].

This study reports the synthesis of 3,6-di-*tert*-butyl-2-hydroxy-4-pyridinylphenolate (LH), a new diolate type redox active ligand, possessing a zwitter-ionic nature, which is retained after the formation of heteroligand tin(IV) complexes. The ligand is characterized by the above-indicated mixed type of binding to the coordination center. Of particular interest is the pronounced solvatochromic effect of these compounds, the causes for which are considered in the paper.

EXPERIMENTAL

Commercial chemicals (Aldrich) were used as received. Organotin compounds [15], 3,6-di-*tert*-butyl-*o*-benzoquinone [16], 3,6-di-*tert*-butylcatechol [17], and 3,6-di-*tert*-butyl-4-chlorocatechol [18] were synthesized by known procedures. The solvents needed for experiments were purified and dehydrated by standard procedures [19].

Synthesis of 3,6-di-*tert*-butyl-2-hydroxy-4-pyridinylphenolate (LH). Method 1. 3,6-Di-*tert*-butyl-*o*-benzoquinone (0.5 g, 2.28 mmol) and 3,6-di-*tert*-butylcatechol (0.1 g, 0.45 mmol) were dissolved in excess

pyridine (25 mL, 0.31 mol) in a flat-bottom flask. The reaction mixture was refluxed with vigorous magnetic stirring for 2 days. The dark red crystals thus formed were collected on a glass filter, washed with heptane, and dried in air. Heptane (10 mL) was added to the filtrate, the resulting solution was kept for 24 h at room temperature, and then the formed bright red powder product was collected on a glass filter, washed with heptane, and dried. The total product yield was 0.32 g (42%).

For $C_{19}H_{25}NO_2$		
Anal. calcd., %	C, 76.22	H, 8.42
Found, %	C, 75.95	H, 8.23

IR (ν, cm^{-1}): 487 w, 538 m, 604 m, 630 w, 641 w, 681 m, 710 s, 720 m, 751 m, 776 m, 789 m, 824 s, 849 m, 867 w, 877 w, 926 w, 953 s, 978 m, 989 w, 1000 w, 1029 m, 1060 w, 1070 w, 1100 w, 1120 s, 1147 w, 1165 m, 1203 m, 1262 s, 1287 s, 1308 s, 1365 s, 1432 s, 1486 m, 1523 m, 1580 m, 1595 w, 1623 s, 1725 w, 1843 w, 1882 w, 2032 w, 2998 m, 3027 w, 3066 w, 3078 m, 3091 m, 3102 w, 3148 w, 3193 w. ^{1}H NMR (400 MHz; CD_3OD; δ, ppm): 1.20 (s, 9H, *t*-Bu); 1.36 (s, 9H, *t*-Bu); 6.19 (s, 1H, H_{arom}); 8.04–8.11 (m, 2H, $H(Py)_\beta$); 8.61–8.69 (m, 1H, $H(Py)_\gamma$); 9.02–9.04 (m, 2H, $H(Py)_\alpha$).

The LH · 0.5Py crystals suitable for X-ray diffraction were prepared by crystallization of 3,6-di-*tert*-butyl-2-hydroxy-4-pyridinylphenolate from hot pyridine.

Synthesis of 1-(2,5-di-*tert*-butyl-3,4-dihydroxyphenyl)pyridinium chloride (LH_2Cl). An excess of pyridine (1 mL, 12.4 mmol) was added to a solution of 4-chloro-3,6-di-*tert*-butylcatechol (1 g, 3.9 mmol) in 2-propanol (20 mL), and then the reaction mixture was refluxed for 2 h under argon. After completion of the reaction, the solvents were removed under reduced pressure, and the dry residue was recrystallized from an acetonitrile–toluene (1 : 1). mixture. The yield of colorless crystals was 0.72 g (55%).

For $C_{19}H_{26}NO_2Cl$		
Anal. calcd., %	C, 67.94	H, 7.80
Found, %	C, 68.22	H, 7.99

IR (ν, cm^{-1}): 528 m, 615 s, 645 s, 675 s, 694 w, 708 m, 733 m, 769 w, 789 s, 810 w, 843 m, 902 m, 945 s, 965 s, 1028 m, 1059 w, 1127 s, 1162 w, 1191 m, 1206 m, 1223 w, 1248 w, 1270 s, 1401 s, 1482 s, 1547 w, 1591 m, 1600 m, 1628 s, 1797 w, 3100 s. ^{1}H NMR (400 MHz; CD_3OD; δ, ppm): 1.22 (s, 9H, *t*-Bu), 1.39 (s, 9H, *t*-Bu), 6.70 (s, 1H), 8.15–8.22 (m, 2H), 8.72–8.79 (tt, J = 7.9, 1.3 Hz, 1H), 9.11–9.17 (m, 2H). ^{13}C NMR (400 MHz; CD_3OD; δ, ppm): 28.35, 28.98, 34.15, 36.47, 117.90, 127.21, 130.14, 133.95, 137.15, 146.68, 147.03, 147.76, 148.06.

Synthesis of 3,6-di-*tert*-butyl-2-hydroxy-4-pyridinylphenolate (LH). Method 2. Potassium *tert*-butoxide (0.18 g, 1.6 mmol) was added with vigorous stirring to a solution of 1-(2,5-di-*tert*-butyl-3,4-dihydroxyphenyl)pyridinium chloride (0.5 g, 1.5 mmol) in 2-propanol (10 mL). The reaction mixture turned bright orange. After completion of the reaction, the solution was cooled to 5°C. The product was filtered off and washed with water (10 mL) and with cooled 2-propanol (10 mL). The dried precipitate was recrystallized from methanol, which gave 0.29 g (0.97 mmol, 65.1%) of the bright-orange powder. The spectral characteristics of the compound were similar to those of 3,6-di-*tert*-butyl-2-hydroxy-4-pyridinylphenolate synthesized by Method 1 (see above).

Synthesis of 3,6-di-*tert*-butyl-2-oxy-4-pyridinylphenolato(triphenyl)tin(IV) (I). Ph_3SnOH (0.11 g, 0.295 mmol) was added to a bright-red solution of LH (0.098 g, 0.295 mmol) in methanol (10 mL), and a pink precipitate was formed almost immediately. After the addition of Et_3N (0.5 mL), the reaction mixture was stirred without heating for 0.5 h. The claret-colored precipitate was collected on a glass filter, washed with methanol, and dried. The yield was 0.18 g (92.3%).

For $C_{37}H_{39}NO_2Sn$		
Anal. calcd., %	C, 68.54	H, 6.06
Found, %	C, 68.77	H, 6.18

IR (ν, cm^{-1}): 505 w, 538 w, 551 w, 575 w, 616 w, 631 w, 654 m, 684 m, 702 s, 729 s, 779 w, 788 m, 815 w, 852 m, 964 m, 985 m, 995 w, 1024 w, 1070 m, 1096 w, 1127 m, 1157 w, 1189 w, 1201 m, 1274 s, 1315 w, 1353 w, 1386 w, 1407 s, 1438 s, 1507 w, 1570 w, 1621 m, 1828 w, 1882 w, 1933 w, 1957 w, 3036 w, 3049 w, 3062 m, 3106 w. ^{1}H NMR (400 MHz; $(CD_3)_2SO$; δ, ppm): 1.16 (s, 9H, *t*-Bu), 1.36 (s, 9H, *t*-Bu), 5.99 (s, 1H, –C=CH–), 7.23–7.30 (m, 9H, –C=CH–), 7.67–7.71 (m, 6H, –C=CH–), 8.02–8.09 (t, 2H, –C=CH–), 8.58–8.65 (t, 1H, –C=CH–), 9.18 (d, 2H, J = 5.78 Hz, –C=CH–).

The red single crystals of **I** · CH_3CN suitable for X-ray diffraction were grown by recrysyallization of the product from acetonitrile, with cooling of the saturated solution being conducted in the absence of oxygen or air moisture.

Synthesis of 3,6-di-*tert*-butyl-2-oxy-4-pyridinylphenolato(diphenyl)chlorotin(IV) (II). Ph_2SnCl_2 (0.10 g, 0.295 mmol) was added to a bright red solution of LH (0.098 g, 0.295 mmol) in methanol (10 mL). The reaction mixture was stirred at room temperature for 1 h, then the solution turned turbid and acquired a bright yellow color. The addition of Et_3N (0.5 mL) resulted in a change in the solution color to red-orange. The

red-orange precipitate that formed was collected on a glass filter, washed with methanol, and dried. The yield was 0.12 g (69.5%).

For $C_{31}H_{34}NO_2ClSn$		
Anal. calcd., %	C, 61.36	H, 5.65
Found, %	C, 61.51	H, 5.72

IR (ν, cm^{-1}): 499 w, 509 m, 525 w, 541 w, 553 w, 588 m, 622 m, 633(s), 655 m, 686 m, 703 s, 739 s, 780 w, 788 m, 815 m, 851 m, 923 w, 961 m, 984 s, 997 w, 1025 w, 1046 m, 1058 s, 1065 s, 1097 w, 1128 s, 1159 m, 1185 w, 1202 m, 1262 s, 1318 m, 1358 w, 1403 s, 1431 m, 1443 s, 1514 w, 1578 m, 1624 m, 1734 w, 1774 w, 1831 w, 1922 w, 3041 w, 3067 m, 3075 w, 3107 m, 3169 m.

^{1}H NMR (400 MHz; $(CD_3)_2SO$; δ, ppm): 1.18 (s, 9H, *t*-Bu), 1.41 (s, 9H, *t*-Bu), 6.07 (s, 1H, –C=CH–), 7.24–7.36 (m, 6H, –C=CH–), 7.68–7.70 (m, 1H, –C=CH–), 7.80–7.85 (m, 3H, –C=CH–), 8.05–8.11 (t, 2H, –C=CH–), 8.60–8.68 (t, 1H, –C=CH–), 9.24 (d, 2H, J = 5.42 Hz, –C=CH).

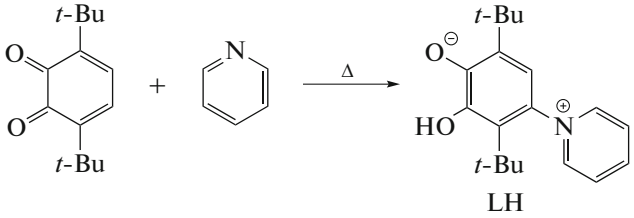
IR spectra were measured in Nujol using KBr cells and FSM-1201 (4000–450 cm^{-1} range) FT IR spectrometers. The NMR spectra were recorded on a Bruker Avance III instrument (400 MHz). The chemical shifts were referred to tetramethylsilane used as the internal standard. Elemental analysis (C, H) was done on an Euro EA 3000 analyzer. Electronic absorption spectra were measured in quartz cells (l = 1 cm) on a PerkinElmer Lambda-25 spectrophotometer (200–1100 nm range). The ESR spectra were run on a Bruker EMX spectrometer (operating at ~9.7 GHz). Diphenyl picryl hydrazide was applied as the standard for determining the g-factor (g = 2.0037).

Single crystal X-ray diffraction study of LH · 0.5Py and **I** · CH_3CN was carried out on a Bruker D8 Quest diffractometer (ω-scan mode, MoK_α-radiation, λ = 0.71073 Å, T = 100 K). The experimental sets of intensities were collected and integrated, the absorption corrections were applied, and structure refinement was performed using APEX2 [20], SADABS [21], and SHELX [22] program packages. The structures were solved by the direct method and refined by full-matrix least squares method on F^2_{hkl} in the anisotropic approximation for nonhydrogen atoms. All hydrogen atoms, except for H(2A) in LH, were placed into geometrically calculated positions and refined isotropically. The H(2A) atom in LH was found from difference Fourier maps and refined in the isotropic approximation. The crystallographic data and X-ray experiment and structure refinement details are summarized in Table 1.

The structures were deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1974166 (LH), 1974165 (**I**); ccdc.cam.ac.uk/structures).

RESULTS AND DISCUSSION

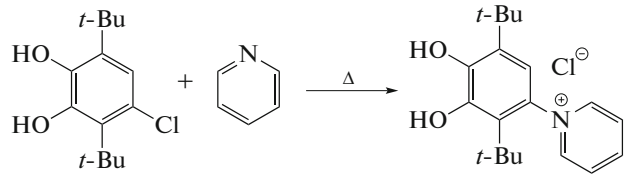
The sterically hindered 3,6-di-*tert*-butyl-*o*-benzoquinone is an important starting compound for the synthesis of *o*-benzoquinone derivatives with various substituents. For example, alkoxy-substituted *o*-benzoquinone ligands were prepared by nucleophilic addition of alcohols [23]. Similarly, reactions of primary amines with 3,6-di-*tert*-butyl-*o*-benzoquinone were used to prepare new ligand systems derived from both *ortho*- and *para*-benzoquinones [24, 25]. The nucleophilic addition of pyridine to 3,6-di-*tert*-butyl-*o*-benzoquinone carried out by refluxing in excess pyridine in the presence of 3,6-di-*tert*-butylcatechol gave 3,6-di-*tert*-butyl-2-hydroxy-4-pyridinylphenolate (LH) according to Method 1 (Scheme 1). This compound is a new diolate type ligand with a zwitterion nature.



Scheme 1.

The reactions of pyridine with halogenated derivatives of dioxolene ligands can be considered as alternative methods for the introduction of pyridinyl moiety into the ligand structure. The examples previously reported in the literature demonstrate that bromine may be replaced by pyridinium using 3,4,5,6-tetrabromocatechol [26], either in the free state or in the radical anion form directly in the cobalt [27] or magnesium [28] coordination sphere. Meanwhile, in the reactions with 3,4,5,6-tetrachlorocatechol, pyridine acts as a base: the electron-withdrawing effect of chlorine atoms increases the ability of the OH groups to be deprotonated; therefore, the major reaction is proton elimination by pyridine. For the preparation of nucleophilic substitution product, the authors proposed a procedure that included the use of *o*-chloranil, pyridine, and $NH_2OH \cdot HCl$ [26, 29].

In the present study, 1-(2,5-di-*tert*-butyl-3,4-dihydroxyphenyl)pyridinium was obtained using pyridine and 4-chloro-3,6-di-*tert*-butylcatechol as the starting reactants (Scheme 2). The nucleophilic substitution reaction of chlorine with pyridine is possible owing to the presence of strong electron-donating *tert*-butyl groups, which counterbalance the electron-withdrawing effect of chlorine.

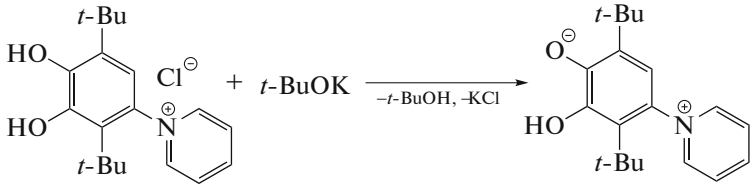


Scheme 2.

Table 1. Crystallographic data and structure refinement details for LH · 0.5Py and **I** · CH_3CN

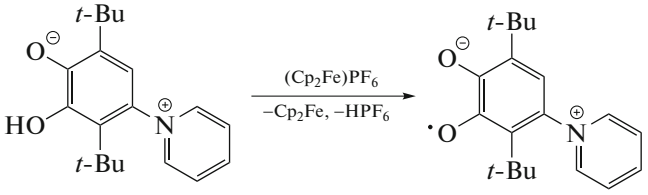
Parameter	Value	
	LH · 0.5Py	**I** · CH_3CN
Molecular formula	$C_{21.50}H_{27.50}N_{1.50}O_2$	$C_{39}H_{42}N_2O_2Sn$
M	338.95	689.43
System	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a, Å	10.8766(5)	12.8581(13)
b, Å	15.6499(8)	19.774(2)
c, Å	12.1013(6)	26.724(3)
β, deg	116.0320(10)	91.615(2)
V, Å^3	1850.88(16)	6792.0(12)
Crystal size, mm	0.16 × 0.11 × 0.10	0.31 × 0.10 × 0.09
$\theta_{max,}$ deg	28.81	28.50
Z	4	8
ρ(calcd.), g/cm^3	1.216	1.348
μ, mm^{-1}	0.078	0.788
F(000)	732	2848
Number of measured reflections	26131	79852
Number of unique reflections (R_{int})	4802 (0.0376)	17147 (0.0571)
Number of refined parameters	251	838
R_1, wR_2 ($I > 2\sigma(I)$)	0.0452, 0.1121	0.0379, 0.0753
R_1, wR_2 (for all data)	0.0613, 0.1211	0.0620, 0.0825
$S(F^2)$	1.038	1.036
Residual electron density (max/min), e/Å^3	0.379/–0.295	1.197/–0.828

Similarly to catechols annulated by dithiocarbamate salts [30], 1-(2,5-di-*tert*-butyl-3,4-dihydroxyphenyl)-pyridinium chloride can react with bases to give LH according to Method 2 (Scheme 3). To summarize the above, ligand LH can be synthesized in two steps using 4-chloro-3,6-di-*tert*-butylcatechol as the starting reactant.



Scheme 3.

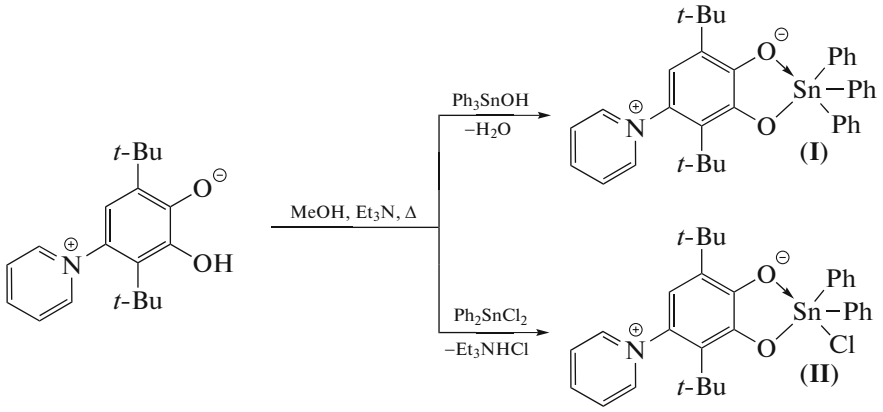
The ligand LH can participate in redox reactions with oxidants such as lead(IV) oxide or ferricinium cation. The reaction of LH with $(Cp_2Fe)PF_6$ in anhydrous methanol is accompanied by appearance of an ESR signal indicating the formation of the corresponding phenoxyl radical (Scheme 4).



Scheme 4.

The hyperfine structure of the ESR spectrum of phenoxyl (1 : 1 doublet of 1 : 1 : 1 triplets) corresponds to coupling of the unpaired electron with the phenoxyl ring proton and with the magnetic nucleus of the pyridinyl nitrogen (Fig. 1). The ESR parameters are as follows: g_i = 2.0045, $a_i(^1H)$ = 0.291 mT, $a_i(^{14}N)$ = 0.067 mT.

The reaction of equimolar amounts of organotin compounds (Ph_3SnOH or Ph_2SnCl_2) with LH in the presence of a base in methanol gives heteroligand five-coordinate tin(IV) complexes **I** and **II** as the final products (Scheme 5). These reactions proceed under aerobic conditions in quantitative yields.



Scheme 5.

The compound LH is a zwitter-ion (Schemes 1 and 3, Fig. 2), in which the N(1) atom is positively charged, while the negative charge is concentrated on the O(1) atom. The central quinoid moiety in LH is virtually planar (the average deviation of atoms from the plane is 0.03 Å). The six-membered carbon ring is much less distorted than that in the initial 3,6-di-*tert*-butyl-*o*-benzoquinone [31]: the C–C bond lengths in LH are in the 1.387(2)–1.432(2) Å range, which is comparable with the bond lengths in the benzene ring (1.40 Å). The C(1)–O(1) distance is 1.308(2) Å, which is markedly shorter than the C–O bond length to the protonated oxygen atom (C(2)–O(2), 1.372(2); O(2)–H(2A), 0.91(2) Å), apparently because of the conjugation of the O(1) lone pair with the aromatic ring π-system. The dihedral angle between the planes of six-membered rings is 78.11(3)°. The geometric characteristics of the pyrinidyl substituent (C–N, 1.348(2), 1.350(2) Å; C–C, 1.375(2)–1.384(2) Å) are comparable with similar characteristics of the pyridine molecule. The N(1)–C(4) bond length is 1.461(2) Å and reflects the donor-acceptor nature of the bond. Despite the non-equivalence of substituents in the 4,5-positions of the carbon ring, the *tert*-butyl groups in LH occur virtually in the eclipsed conformation.

Complex **I** crystallizes in the monoclinic space group $P2_1/c$. The independent part of the unit cell contains two crystallographically independent molecules **IA** and **IB** with similar geometric characteristics (the molecular structure of **I** is shown in Fig. 3). In each molecule, the metal center is linked to two oxygen atoms of LH and to three carbon atoms of the phenyl groups. Thus, the formal coordination number of Sn(IV) in **I** is five. Note that the relative positions of ligands in **IA** and **IB** are somewhat different. Indeed, whereas the Sn(IV) coordination polyhedron in **IB** can be described as a highly distorted trigonal bipyramid (τ_5 = 0.64 [32]) whose apical positions are occupied by C(20B) and O(1B) atoms, the coordination geometry of Sn(IV) in **IA** (Fig. 4) is intermediate between a tetragonal pyramid and a trigonal bipyramid (τ_5 = 0.53 [32]). Also, the position of the C(26) phenyl substituents in molecules **IA** and **IB** are somewhat different. In **IA**, the O(2)Sn(1)C(26)C(27) torsion angle is 171.0(2)° and is markedly greater than the similar angle in **IB** (113.3(2)°).

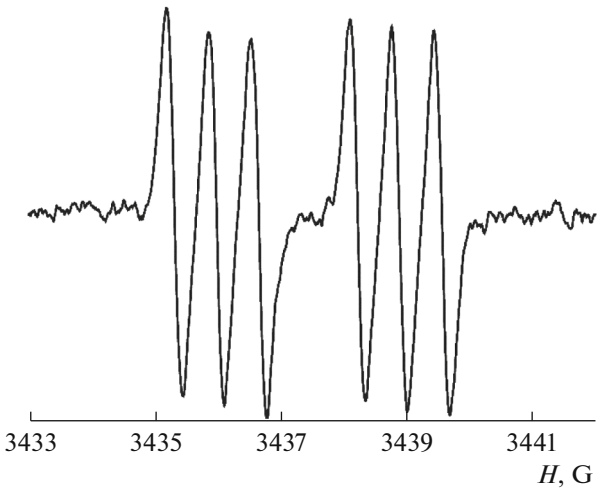


Fig. 1. ESR spectrum of the phenoxyl radical formed upon the oxidation of LH.

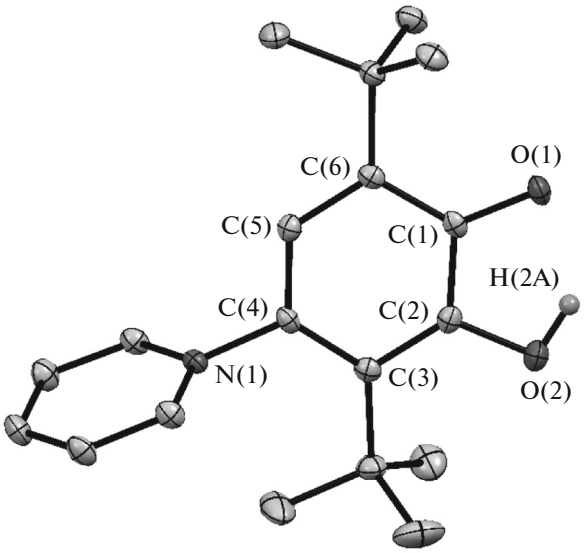


Fig. 2. Molecular structure of LH. The thermal ellipsoids of atoms are drawn at the 50% probability level. The hydrogen atoms (except H(2A)) are omitted for clarity.

The ligands LH are unsymmetrically coordinated by Sn(IV) ions. The Sn(1)–O(2) bond lengths (2.071(2), 2.059(2) Å) are shorter than the sum of covalent radii of these elements (2.09 Å) [33] and, hence, these contacts can be classified as covalent bonds. The Sn(1)–O(1) distances are much longer (2.170(2), 2.178(2) Å), but do not exceed the sum of van der Waals radii of tin and oxygen atoms (3.70 Å) [33], indicating the donor-acceptor nature of the contacts. Previously, it was shown that this coordination mode of *o*-benzoquinone ligands is also present in hydroxy-paraquinone derivatives; however, in all known cases, the ligand was not zwitter-ionic [13, 14]. Unlike the C–O distances in LH, which are markedly different (1.308(2), 1.372(2) Å), these bond lengths in complex **I** differ little and occur in a narrow range of 1.316(3)–1.339(3) Å. The N–C and C–C bond lengths in the central six-membered ring of the ligand and the pyridinyl substituent in **I** are comparable with analogous characteristics of the LH molecule (Table 2). Generally, the oxidative state of the ligand in **I** corresponds to the catecholate redox form of *o*-benzoquinone [34]. The pyrinidyl substituent is arranged almost orthogonally to the quinoid moiety of the ligand: the dihedral angle between the six-membered ring planes is somewhat larger than that in LH (78.11(3)°) and is 88.28(8)° (**IA**) and 83.76(8)° (**IB**). Like in LH, the *tert*-butyl substituents in **I** are in the eclipsed conformation.

The electronic absorption spectra of LH and complexes **I** and **II** with this ligand were measured under aerobic conditions in the 200–1100 nm wavelength range. The measurements were carried out for a broad range of solvents (Table 3) in which the test compounds demonstrated a sufficient solubility for conducting the experiment.

It was found that the ligand and the metal complexes exhibit a pronounced solvatochromic effect in the visible and near ultraviolet ranges of the electronic spectrum. In order to elucidate the cause for solvatochromism, various properties of solvents were considered: ε_r, μ, n_D^{20}, E_T^N, DN^N, and AN. Solvent polarity was found to be the key characteristics of the medium that caused the change in the electronic spectrum. The observed blue shift of the spectra of the LH ligand

Table 2. Selected bond lengths (Å) of compounds LH and **I**

Bond	**I**	Bond	LH	**I**	Bond	LH	**I**
Sn(1)–O(1)	2.170(2)	O(2)–H(2A)	0.91(2)		N(1)–C(4)	1.461(2)	1.464(3)
	2.178(2)	O(1)–C(1)	1.308(2)	1.316(3)			1.461(3)
Sn(1)–O(2)	2.071(2)			1.319(3)	N(1)–C(15)	1.348(2)	1.341(3)
	2.059(2)	O(2)–C(2)	1.372(2)	1.324(3)			1.337(3)
Sn(1)–C(20)	2.180(2)			1.339(3)	N(1)–C(19)	1.350(2)	1.341(3)
	2.190(2)	C(1)–C(2)	1.432(2)	1.429(3)			1.338(2)
Sn(1)–C(26)	2.128(3)			1.414(3)	C(15)–C(16)	1.376(2)	1.371(3)
	2.137(3)	C(2)–C(3)	1.392(2)	1.402(3)			1.367(4)
Sn(1)–C(32)	2.140(3)			1.403(3)	C(16)–C(17)	1.384(2)	1.380(4)
	2.146(3)	C(3)–C(4)	1.409(2)	1.393(3)			1.375(4)
				1.396(3)	C(17)–C(18)	1.382(2)	1.376(4)
		C(4)–C(5)	1.387(2)	1.394(3)			1.373(4)
				1.386(3)	C(18)–C(19)	1.375(2)	1.371(3)
		C(5)–C(6)	1.395(2)	1.389(3)			1.368(3)
				1.386(3)			
		C(1)–C(6)	1.410(2)	1.398(3)			
				1.403(3)			

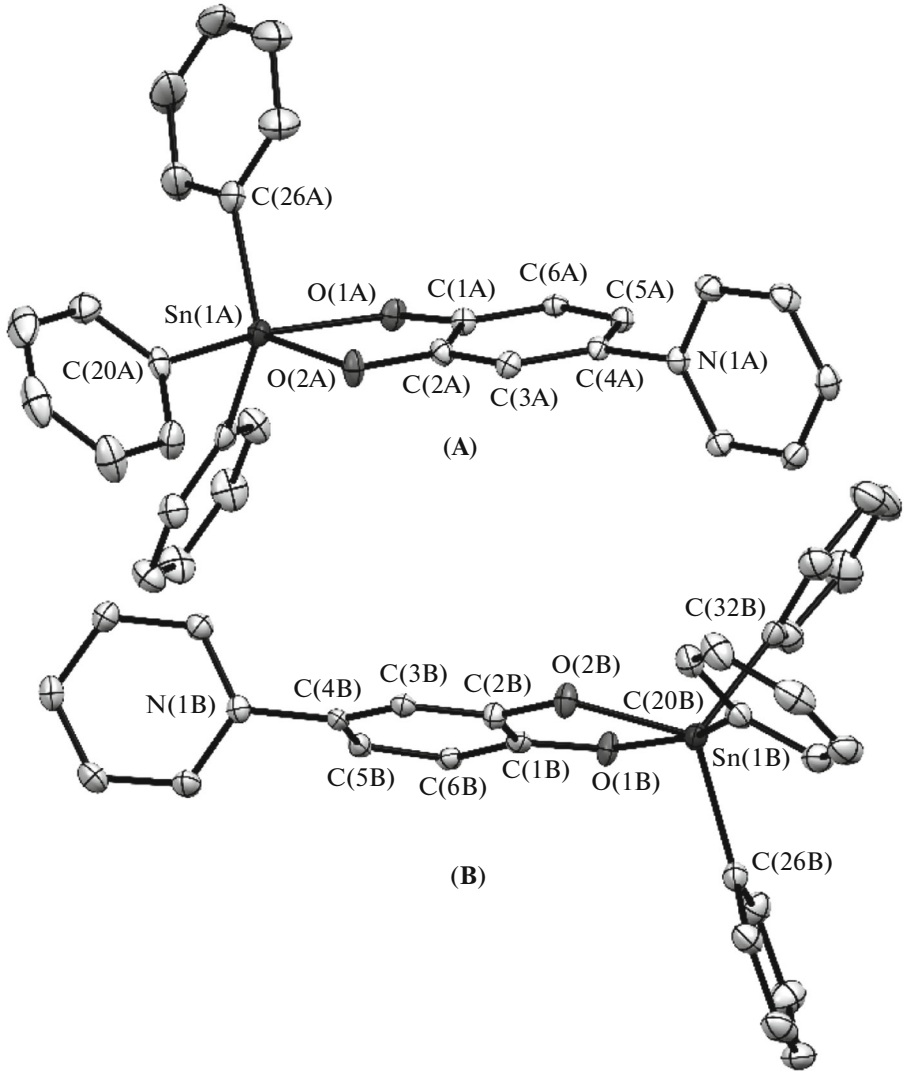


Fig. 3. Molecular structure of compound **I** (crystallographically independent molecules **A** and **B**). The thermal ellipsoids of atoms are drawn at the 50% probability level. The hydrogen atoms and *tert*-butyl groups are omitted for clarity.

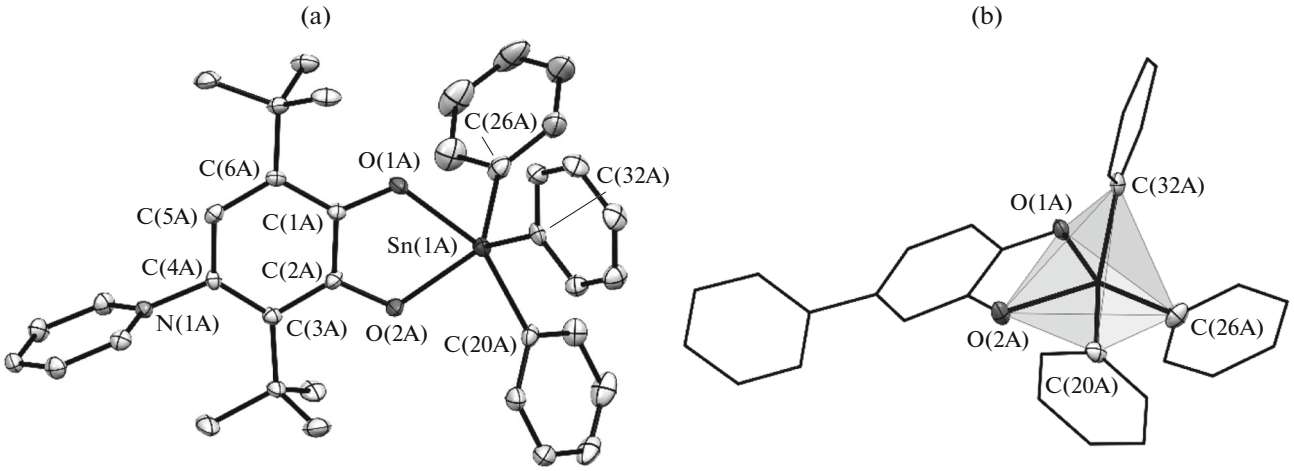


Fig. 4. (a) Molecular structure of compound **IA** and (b) Sn(1A) coordination polyhedron. The thermal ellipsoids of atoms are drawn at the 50% probability level. The hydrogen atoms (a, b) and *tert*-butyl groups (b) are omitted for clarity.

Table 3. Positions (λ, nm) of the longest-wavelength absorption maxima in the spectra of LH, **I**, and **II**

Solvent	LH	Solvent	**I**	**II**
Acetic acid	317	Dimethyl sulfoxide	481	458
Methanol	451	Dimethylformamide	487	464
Ethanol	465	Acetonitrile	491	463
2-Propanol	497	Acetone	509	482
Dimethylformamide	530	Tetrahydrofuran	541	510
Dimethyl sulfoxide	531	Dichloromethane	561	535

(Fig. 5, *2–6*), which have similar shape, corresponds to increasing solvent polarity. The position of the longest-wavelength maximum is well correlated with the normalized empirical polarity parameter E_T^N (Fig. 6a).

This characteristics was proposed by Dimroth and Reichardt [35] and describes the energy of electron transition (at $T = 25°C$) corresponding to the long-wavelength absorption of the standard *N*-phenoxypyridinium betaine dye, which is structurally similar to LH. Another factor responsible for the solvatochromism of LH is the acceptor capacity (electrophilicity) of the solvent. The increase in the acceptor number (AN), characterizing the Lewis acidity of the solvent [35], induces a shift of the electronic absorption spectrum to shorter wavelengths. In view of the zwitterionic character of the ligand, the crucial factor in this case is evidently the ability of the solvent to efficiently solvate the negatively charged oxygen atom of LH. It is noteworthy that the pattern of the electronic spectrum of LH recorded in acetic acid (Fig. 5, *1*) differs substantially from the spectra presented above (Fig. 5, *2–6*) and the absorption peaks do not follow the trend (Fig. 6a). It is evident that in acetic acid, the negatively charged oxygen atom is protonated to give a pyridinium salt, similar to LH_2Cl.

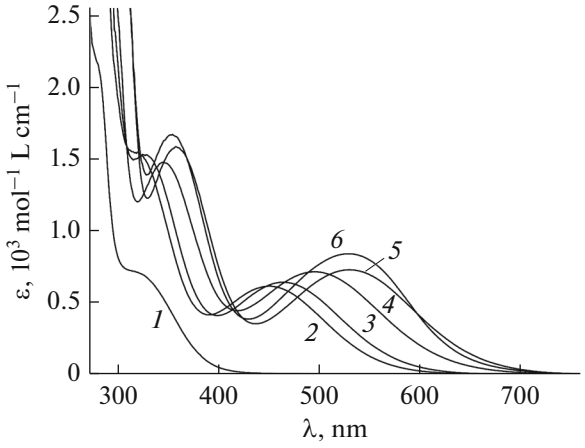


Fig. 5. Electronic absorption spectrum of LH measured in (*1*) acetic acid, (*2*) methanol, (*3*) ethanol, (*4*) 2-propanol, (*5*) dimethylformamide, and (*6*) dimethyl sulfoxide.

The solvent polarity is also the crucial factor for the solvatochromism observed for tin(IV) complexes **I** and **II** (Fig. 7). In this case, the blue shift of the longest-wavelength absorption bands is best correlated (Fig. 6b) with the increase in the polarity index *P'* of the solvent, which was proposed by Snyder [36] and takes account of the overall ability of the solvent to proton donor, proton acceptor, and dipole–dipole interactions with the solute. It is noteworthy that metal complexes **I** and **II** demonstrate similar electronic spectral patterns and the type of solvatochromic effect. The replacement of one phenyl group at the metal atom by a halogen induces short-wavelength shifts of the absorption bands, generally by more than 20 nm (Table 3), which makes the LH ligand a convenient test platform for estimating the electronic properties of substituents in coordination and organoelement compounds.

As a result of this study, we developed two synthetic approaches towards a new diolate type zwitter-ionic redox-active ligand. The complex forming properties were tested in relation to tin(IV) organic derivatives. It was found that the solvatochromic effect inherent in the initial ligand is also retained for the complexes. The electronic absorption spectra of the obtained compounds proved to be highly sensitive to charge distribution in the molecules.

CONFLICT OF INTEREST

The authors declare that they have no conflicst of interest.

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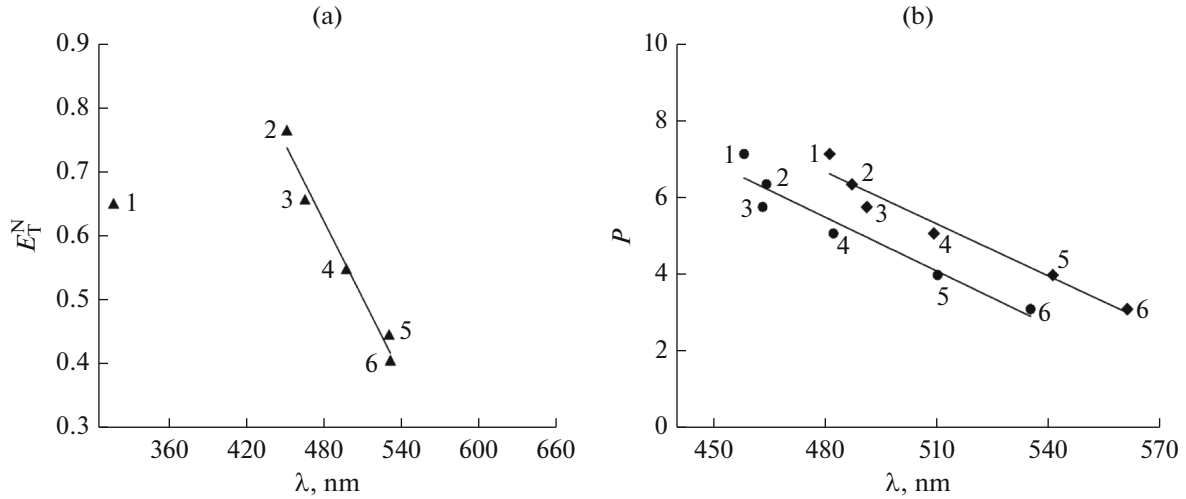

Fig. 6. (a) E_T^N/λ dependence for LH. Solvents: (1) acetic acid, (2) methanol, (3) ethanol, (4) 2-propanol, (5) dimethylformamide, and (6) dimethyl sulfoxide. (b) P/λ dependence for complexes (rhombuses) **I** and (circles) **II**. Solvents: (1) dimethyl sulfoxide, (2) dimethylformamide, (3) acetonitrile, (4) acetone, (5) tetrahydrofuran, and (6) dichloromethane.

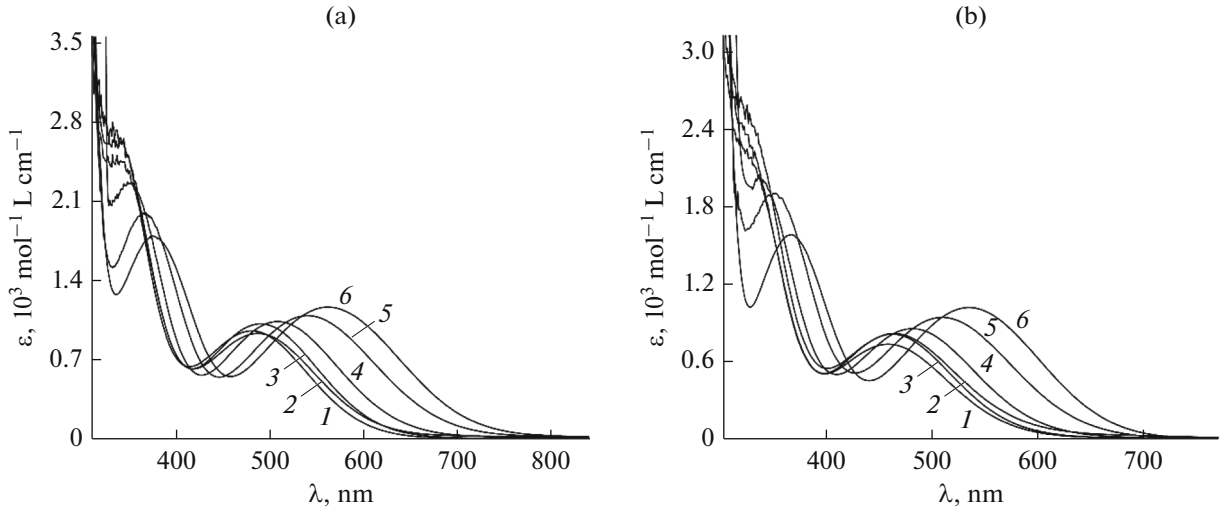

Fig. 7. Electronic absorption spectra of tin(IV) complexes (a) **I** and (b) **II** measured in (*1*) dimethyl sulfoxide, (*2*) dimethylformamide, (*3*) acetonitrile, (*4*) acetone, (*5*) tetrahydrofuran, and (*6*) dichloromethane.

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