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The issue is dedicated to the 70th birthday of Academician V.I. Ovcharenko

Pentacoordinated Complexes of Triphenyltin(IV) with Bidentate *N*-Phenyl-*o*-iminophenols

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Abstract—The reactions of functionalized *o*-iminophenols L^1H–L^5H (L^1H is 2-benzylideneaminophenol, L^2H is 2-benzylideneamino-5-methylphenol, L^3H is 2-benzylideneamino-5-chlorophenol, L^4H is 2-benzylideneamino-3-nitrophenol, and L^5H is 2-benzylideneamino-4-nitrophenol) with triphenyltin(IV) bromide in the presence of the base afford the corresponding triphenyltin complexes **I**–**V** with *o*-iminophenolate ligands of the general form $(L^n)SnPh_3$. The molecular structures of complexes **II** and **III** in the crystalline form are determined by X-ray diffraction (CIF files CCDC № 2131549 (**II**) and 2131548 (**III**)).

Keywords: Schiff base, *o*-iminophenolate, tin(IV), X-ray diffraction

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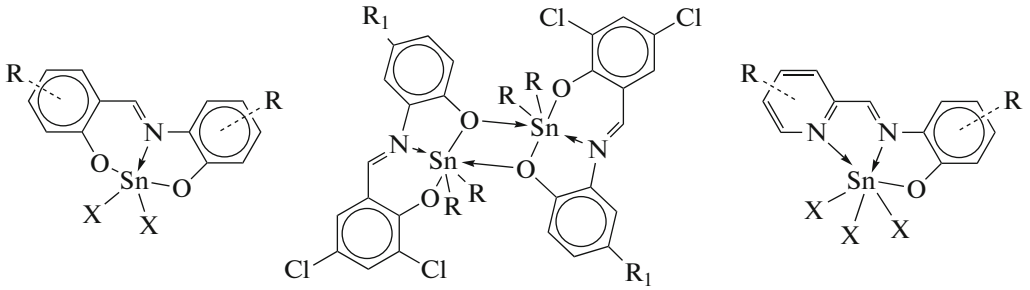
INTRODUCTION

Metal complexes with Schiff bases play an important role in the modern coordination chemistry [1–6]. At present, the coordination compounds of transition metals with ligands of this class are well studied, on the one hand, due to simplicity of their synthesis and, on the other hand, owing to broad possibilities of functionalization provided by Schiff bases that serve as ligands. These complexes find use in various fields of chemistry and technology and are promising objects in biochemical and medical research [7–14].

Among the complexes of the main subgroup metals with Schiff bases, special attention is given to the tin complexes [15–19]. These compounds are efficient fungicides, pesticides, aerosols, and anticancer agents and, in addition, they can act as active catalysts. The tin complexes with the Schiff bases are objects of comprehensive studies of the light emitting and optical properties is caused by a high emission ability of the complexes and their good thermal stability [20–23]. The complexes are also attractive from the viewpoint of variety of structural motifs. The tin(IV) complexes with the Schiff bases exhibit the antibacterial, antifungal, and anticancer effects in pharmacology and are model objects for studying a broad range of biochemical activity [24–28].

Among the tin(IV) complexes with the *o*-iminophenolate Schiff bases, the compounds based on the tridentate O,N,O-, O,N,S-, and O,N,N-ligands (Scheme 1) are presented most widely [23, 29–36].



[23, 29–33] [34] [35, 36]

Scheme 1.

However, data on the tin complexes with the bidentate iminophenolate ligands are presented by a considerably less number of publications, for example, the tin(IV) complex with *N*-benzylidene-*o*-anisidine [37] and tin(II) and tin(IV) bis(iminophenolates) based on the ferrocene-containing Schiff bases [38–40]. In this work, triphenyltin(IV) *o*-iminophenolates based on substituted 2-benzylideneaminophenols were synthesized. The crystal structures of (2-benzylideneamino-5-methylphenolato)triphenyltin(IV) and (2-benzylideneamino-5-chlorophenolato)triphenyltin(IV) were determined by X-ray diffraction (XRD).

EXPERIMENTAL

All procedures on the synthesis of the tin complexes with the *o*-iminophenolate ligands were carried out in the absence of air oxygen and moisture. The solvents used in the syntheses were purified and dehydrated using standard procedures [41, 42]. Commercially available reagents (*o*-aminophenols, benzaldehyde, 2-pyridinealdehyde, triphenyltin bromide, and triethylamine) were used as received.

^{1}H NMR spectra were recorded on Bruker Avance DPX-200 (200 MHz) spectrometers. For NMR spectra recording, $CDCl_3$ and DMSO-d_6 were used. IR spectra in a range of 400–4000 cm^{-1} were detected in Nujol on an FSM-1201 spectrometer with Fourier transform. The molecular structures of the complexes in the crystalline state were determined using Bruker D8 Quest (100 K) and Agilent Xcalibur single-crystal diffractometers.

General procedure for the synthesis of ligands L^1H–L^5H based on substituted and unsubstituted *o*-aminophenols and benzaldehyde. Substituted *o*-aminophenol (1 equiv) was dissolved in methanol (100 mL). The corresponding aromatic aldehyde (1 equiv) was added dropwise to the resulting solution at room temperature. The reaction mixture was refluxed for several hours with permanent stirring and then left to stay at −18°C overnight. The formed precipitate was filtered off, washed with cold methanol, and dried in air.

2-Benzylideneaminophenol (L^1H): a finely crystalline yellow powder was obtained from benzaldehyde (1.85 mL, 18 mmol) and 2-aminophenol (2 g, 18 mmol). The yield was 2.48 g (69%).

IR (Nujol; ν, cm^{-1}): 3328 s, 3059 w, 3041 w, 3019 w, 2953 w, 2923 s, 2854 s, 2729 w, 1940 w, 1906 w, 1625 s, 1584 s, 1574 s, 1482 s, 1450 m, 1359 w, 1314 w, 1290 s, 1251 s, 1197 m, 1168 m, 1148 m, 1102 w, 1072 w, 1026 m, 999 w, 968 m, 936 w, 918 w, 895 w, 875 w, 846 m, 790 m, 766 s, 735 m, 689 s, 646 s, 566 w, 502 s, 486 m.

^{1}H NMR ($CDCl_3$; δ, ppm): 6.92 (m, 1H, C_6H_4), 7.00–7.13 (m, 1H, C_6H_4), 7.20 (dd, 1H, C_6H_4), 7.30 (m, 1H, C_6H_4), 7.50 (m, 3H, Ph), 7.93 (m, 2H, Ph), 8.69 (s, 1H, –HC=N–).

2-Benzylideneamino-5-methylphenol (L^2H): a finely crystalline yellow sample of the ligand was obtained from benzaldehyde (0.82 mL, 8 mmol) and 2-amino-5-methylphenol (1 g, 8 mmol). The yield was 0.96 g (58%).

IR (Nujol; ν, cm^{-1}): 3397 s, 3059 w, 3034 w, 2953 w, 2924 s, 2855 s, 2729 w, 1892 w, 1874 w, 1628 s, 1579 s, 1531 w, 1499 s, 1332 s, 1295 m, 1260 m, 1243 w, 1221 m, 1184 m, 1170 w, 1156 s, 1123 w, 1100 w, 1072 m, 1025 w, 1007 m, 967 s, 944 s, 870 s, 801 s, 763 s, 692 s, 628 w, 619 w, 584 s, 512 s, 480 m.

^{1}H NMR ($CDCl_3$; δ, ppm): 2.35 (s, 3H, CH_3), 6.72 (d, 1H, C_6H_3), 6.86 (s, 1H, C_6H_3), 7.24 (d, 1H, C_6H_3), 7.49 (m, 3H, Ph), 7.91 (m, 2H, Ph), 8.68 (s, 1H, –HC=N–).

2-Benzylideneamino-5-chlorophenol (L^3H): a finely crystalline gray-brown powder was obtained from benzaldehyde (0.7 mL, 6.96 mmol) and 2-amino-5-chlorophenol (1 g, 6.96 mmol). The yield was 0.56 g (35%).

IR (Nujol; ν, cm^{-1}): 3329 s, 3082 w, 3061 w, 2953 w, 2922 s, 2847 s, 1878 w, 1711 w, 1628 s, 1600 w, 1582 s, 1533 w, 1518 w, 1480 m, 1451 m, 1333 s, 1313 w, 1280 s, 1256 m, 1236 w, 1222 s, 1182 m, 1114 w, 1071 s, 1022 w, 999 w, 970 s, 940 w, 906 s, 872 m, 857 s, 843 w, 812 s, 758 s, 689 s, 609 w, 585 s, 511 s.

^{1}H NMR ($CDCl_3$; δ, ppm): 7.03 (d, 1H, C_6H_3), 7.26 (d, 1H, C_6H_3), 7.32 (s, 1H, C_6H_3), 7.51 (m, 3H, Ph), 7.91 (m, 2H, Ph), 8.68 (s, 1H, –N=CH–).

2-Benzylideneamino-3-nitrophenol (L^4H): a finely crystalline red powder was obtained from benzaldehyde (0.26 mL, 2.60 mmol) and 2-amino-3-nitrophenol (0.4 g, 2.60 mmol). The yield was 0.44 g (69%).

IR (Nujol; ν, cm^{-1}): 3508 s, 3397 m, 3099 w, 2953 w, 2923 s, 2855 s, 2725 w, 1902 w, 1844 w, 1787 w, 1687 m, 1636 s, 1588 s, 1529 s, 1438 m, 1410 w, 1375 w, 1351 s, 1250 s, 1201 w, 1168 s, 1081 w, 1072 w, 1028 w, 944 w, 901 w, 846 s, 792 s, 735 s, 710 w, 685 w, 668 w, 654 w, 635 w, 595 w, 560 w, 500 m.

^{1}H NMR (DMSO-d_6; δ, ppm): 6.47 (dd, 1H, C_6H_3), 6.76–6.97 (m, 3H, C_6H_3, Ph), 7.39–7.55 (m, 2H, Ph), 7.88–7.99 (m, 1H, Ph), 8.26 (s, 1H, –N=CH–), 10.43 (s, 1H, OH).

2-Benzylideneamino-4-nitrophenol (L^5H): a finely crystalline gray powder was obtained from benzaldehyde (0.26 mL, 2.60 mmol) and 2-amino-4-nitrophenol (0.4 g, 2.60 mmol). The yield was 0.35 g (55%).

IR (Nujol; ν, cm^{-1}): 3317 m, 3110 w, 3078 w, 2953 w, 2921 s, 1968 w, 1899 w, 1787 w, 1691 w, 1629 s, 1578 s, 1510 s, 1484 w, 1444 w, 1353 s, 1298 m, 1271 s, 1242 w, 1202 m, 1176 w, 1154 s, 1119 w, 1087 w, 1025 w, 999 w, 981 m, 946 w, 894 s, 873 m, 828 s, 803 w, 764 s, 746 s, 685 s, 665 w, 636 s, 590 m, 544 w, 494 s, 471 m.

^{1}H NMR ($CDCl_3$; δ, ppm): 7.11 (d, 1H, C_6H_3), 7.56 (dd, 3H, Ph), 7.77 (s, 1H, C_6H_3), 7.97 (d, 2H, Ph), 8.15 (d, 1H, C_6H_3), 8.26 (s, 1H, –N=CH–), 8.82 (s, 1H, OH).

Synthesis of (2-benzylideneaminophenolato)triphenyltin(IV) (L^1)$Sn^{IV}Ph_3$ (I). A solution of ligand L^1H (4.1 mmol, 0.8 g) in toluene (25 mL) was poured to a solution of Ph_3SnBr (4.1 mmol, 1.75 g) in the same solvent (10 mL). Triethylamine (4.1 mmol, 0.56 mL) was added to the resulting solution, and the reaction mixture was stirred for 2 h. The solution was filtered from a precipitate of $[Et_3NH]Br$ and left at –18°C overnight. A yellow finely crystalline precipitate of complex **I** was filtered off and dried in vacuo. The complex is sensitive to air moisture in a solution and stable in the crystalline state. The yield was 1.31 g (59%).

For $C_{31}H_{25}NOSn$

Anal. calcd., %	C, 68.16	H, 4.61	Sn, 21.73
Found, %	C, 67.99	H, 4.50	Sn, 21.97

IR (Nujol; ν, cm^{-1}): 3062 w, 3019 w, 2952 w, 2924 s, 2854 s, 1907 w, 1828 w, 1605 w, 1587 m, 1574 m, 1561 w, 1492 w, 1477 s, 1464 w, 1453 w, 1428 s, 1279 w, 1257 m, 1248 m, 1191 w, 1170 w, 1158 w, 1113 w, 1074 m, 1060 w, 1043 w, 1022 w, 996 w, 968 w, 939 w, 915 w, 873 m, 797 m, 762 s, 734 s, 700 s, 689 s, 658 w, 625 w, 574 w, 536 w, 514 w, 478 w, 454 w.

^{1}H NMR ($CDCl_3$; δ, ppm): 6.93 (d, 1H, C_6H_4), 7.02 (d, 1H, C_6H_4), 7.16 (d, 1H, C_6H_4), 7.30 (dd, 1H, C_6H_4), 7.30–7.97 (m, 20H, arom., $SnPh_3$, C_6H_5), 8.71 (s, 1H, –CH=N–). ^{119}Sn NMR (148 MHz; $CDCl_3$; 25°C; δ, ppm): –127.41.

Synthesis of (2-benzylideneamino-5-methylphenolato)triphenyltin(IV) (L^2)$Sn^{IV}Ph_3$ (II). A solution of ligand L^2H (0.95 mmol, 0.2 g) in toluene (15 mL) was poured to a solution of Ph_3SnBr (0.95 mmol, 0.408 g) and Et_3N (0.95 mmol, 0.13 mL) in the same solvent (25 mL). The reaction mixture was stirred at 35°C for 2 h. The resulting solution was filtered from a precipitate of $[Et_3NH]Br$, toluene was replaced by hexane (15 mL), and the mixture was repeatedly filtered. Thus obtained dark yellow precipitate was dried in vacuo. The yield of complex **II** was 0.316 g (60%). Recrystallization from hexane gave yellow single crystals of the complex suitable for XRD.

For $C_{32}H_{27}NOSn$

Anal. calcd., %	C, 68.60	H, 4.86	Sn, 21.19
Found, %	C, 68.69	H, 4.94	Sn, 20.99

IR (Nujol; ν, cm^{-1}): 3064 s, 3036 w, 3019 w, 2953 w, 2923 s, 2855 s, 2720 w, 2599 w, 1953 w, 1881 w, 1822 w, 1754 w, 1609 s, 1593 m, 1574 s, 1564 w, 1481 s, 1430 s, 1414 m, 1365 w, 1331 w, 1303 s, 1270 w, 1261 s, 1228 w, 1189 s, 1173 m, 1158 s, 1123 s, 1076 s, 1062 w, 1022 w, 1010 w, 997 m, 955 s, 926 w, 912 w, 885 m, 859 s, 811 w, 790 s, 754 s, 698 s, 659 m, 624 s, 586 s, 504 s, 479 w.

^{1}H NMR ($CDCl_3$; δ, ppm): 2.35 (s, 3H, CH_3), 6.73 (dd, 1H, C_6H_3), 6.86 (d, 1H, C_6H_3), 7.24 (d, 1H, C_6H_3), 7.11–8.01 (m, 20H, arom., $SnPh_3$, Ph), 8.69 (s, 1H, –CH=N–). ^{119}Sn NMR (148 MHz; $CDCl_3$; 25°C; δ, ppm): –132.45.

Synthesis of (2-benzylideneamino-5-chlorophenolato)triphenyltin(IV) (L^3)$Sn^{IV}Ph_3$ (III). A solution of ligand L^3H (0.6 mmol, 0.14 g) in THF (15 mL) was poured to a solution of Ph_3SnBr (0.6 mmol, 0.26 g) in the same solvent (20 mL). Triethylamine (0.6 mmol, 0.08 mL) was added to the reaction mixture, and the mixture was stirred at 40°C for 2 h. The formed precipitate of $[Et_3NH]Br$ was removed by filtration. The solvent was replaced by toluene (15 mL), and yellow crystals of complex **III** suitable for XRD were isolated after the solution was held at –18°C for 12 h. The complex in a solution is sensitive to air moisture and stable in the crystalline state. The yield was 0.105 g (30%).

For $C_{31}H_{24}NOClSn$

Anal. calcd., %	C, 64.12	H, 4.17	Sn, 20.44
Found, %	C, 64.23	H, 4.25	Sn, 20.27

IR (Nujol; ν, cm^{-1}): 3330 m, 3136 w, 3065 m, 3052 w, 3005 w, 2952 w, 2924 s, 2853 s, 2725 w, 2646 w, 2595 w, 2350 w, 2144 w, 2094 w, 1981 w, 1959 w, 1883 w, 1823 w, 1766 w, 1713 w, 1628 s, 1601 w, 1576 s, 1534 w, 1479 s, 1451 w, 1429 s, 1410 w, 1332 s, 1313 w, 1303 w, 1280 m, 1258 m, 1236 w, 1224 s, 1182 m, 1158 w, 1116 w, 1021 s, 996 s, 971 s, 940 w, 921 w, 906 s, 872 w, 857 s, 812 s, 790 w, 758 m, 695 s, 678 w, 662 w, 610 w, 586 s, 511 s.

Synthesis of (2-benzylideneamino-3-nitrophenolato)triphenyltin(IV) (L^4)$Sn^{IV}Ph_3$ (IV). A solution of ligand L^4H (1.24 mmol, 0.30 g) in THF (15 mL) was poured to a solution of Ph_3SnBr (1.24 mmol, 0.53 g) in the same solvent (20 mL). Triethylamine (1.24 mmol, 0.17 mL) was added to the reaction mixture, and the mixture was stirred at 40°C for 2 h. The formed precipitate of $[Et_3NH]Br$ was removed by filtration, and THF was replaced by a hexane–ether mixture (20 mL). A tarry vinous-colored precipitate was formed after the solution was held at –18°C for 12 h and then was dissolved in THF again. An undissolved finely crystalline orange powder of compound **IV** was filtered off and dried in vacuo. The yield was 0.053 g (7%).

For $C_{31}H_{24}N_2O_3Sn$

Anal. calcd., %	C, 62.97	H, 4.09	Sn, 20.08
Found, %	C, 63.09	H, 4.16	Sn, 19.89

IR (Nujol; ν, cm^{-1}): 3067 w, 3044 w, 2953 w, 2924 s, 2854 m, 2726 w, 1954 w, 1920 w, 1890 w, 1819 w, 1608 m, 1575 m, 1497 m, 1479 m, 1429 m, 1353 w, 1334 w, 1298 s, 1191 w, 1169 m, 1125 w, 1089 w, 1076 m, 1022 w, 996 m, 948 w, 922 w, 902 m, 878 m, 857 m, 838 m, 759 w, 750 w, 696 s, 674 m, 659 w, 646 w, 617 w, 569 w, 539 w, 499 m.

^{1}H NMR ($CDCl_3$; δ, ppm): 7.38 (dd, 2H, C_6H_3), 7.67 (d, 1H, C_6H_3), 7.30–8.01 (m, 20H, arom., $SnPh_3$, Ph), 8.83 (s, 1H, –HC=N–).

Synthesis of (2-benzylideneamino-4-nitrophenolato)triphenyltin(IV) (L^5)$Sn^{IV}Ph_3$ (V). A solution of ligand L^5H (0.21 mmol, 0.050 g) in THF (15 mL) was poured to a solution of Ph_3SnBr (0.21 mmol, 0.90 g) in the same solvent (20 mL). Triethylamine (0.21 mmol, 0.03 nm) was added to the reaction mixture, and the mixture was stirred at 40°C for 2 h. The formed precipitate of $[Et_3NH]Br$ was removed by filtration. The formation of a tarry precipitate was observed after the solvent was evaporated. A finely crystalline precipitate of compound **V** was formed after dissolution in pentane (20 mL), filtered off, and dried in vacuo. The yield was 0.053 g (4%).

For $C_{31}H_{24}N_2O_3Sn$

Anal. calcd., %	C, 62.97	H, 4.09	Sn, 20.08
Found, %	C, 63.15	H, 4.22	Sn, 19.80

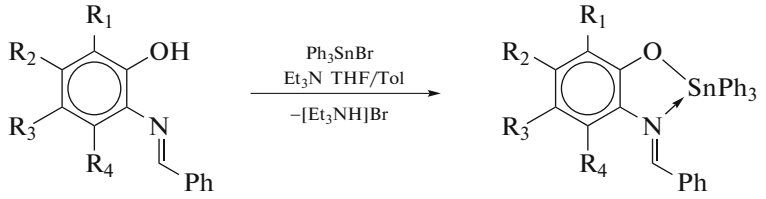
IR (Nujol; ν, cm^{-1}): 3346 w, 3104 w, 3065 w, 3046 w, 2952 w, 2923 s, 2854 s, 1629 m, 1579 s, 1512 s, 1479 w, 1465 m, 1430 w, 1377 w, 1349 s, 1273 s, 1154 w, 1075 w, 1023 w, 997 w, 981 w, 948 w, 893 w, 873 w, 828 w, 802 w, 791 w, 761 w, 746 m, 730 m, 697 m, 685 w, 650 w, 631 w, 590 w, 545 w, 493 w, 472 w.

XRD of compounds **II** and **III** was carried out on Bruker D8 Quest (**II**) and Rigaku OD Xcalibur E (**III**) diffractometers. Experimental sets of intensities were measured and integrated, an absorption correction was applied, and structures were solved and refined using the APEX3 [43], CrysAlis^{Pro} [44], SADABS [45], and SHELX [46] software. The structures were solved using the dual-space algorithm [47] and refined by full-matrix least squares for F^2_{hkl} in the anisotropic approximation for non-hydrogen atoms. Hydrogen atoms in complexes **II** and **III** were placed in geometrically calculated positions and refined isotropically with fixed thermal parameters $U(H)_{iso} = 1.2U(C)_{equiv}$ ($U(H)_{iso} = 1.5U(C)_{equiv}$ for methyl groups). The crystallographic data and XRD and structure refinement parameters are given in Table 1.

The structures were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 2131549 (**II**) and 2131548 (**III**); ccdc.cam.ac.uk/structures).

RESULTS AND DISCUSSION

Tin(IV) complexes **I**–**V** with the phenol-containing Schiff bases of the general formula $(L^n)SnPh_3$, where n = 1–5 (corresponds to the number of the ligand), were synthesized by the exchange reaction of the corresponding *o*-iminophenol L^1H–L^5H with triphenyltin bromide in the equimolar ratio in a solution of toluene or THF in the presence of triethylamine (1 equiv) (Scheme 2).



L^1H: $R_1 = R_2 = R_3 = R_4 = H$
L^2H: $R_1 = R_3 = R_4 = H$, $R_2 = CH_3$
L^3H: $R_1 = R_3 = R_4 = H$, $R_2 = Cl$
L^4H: $R_1 = R_2 = R_3 = H$, $R_4 = NO_2$
L^5H: $R_1 = R_2 = R_4 = H$, $R_3 = NO_2$

$(L^1)SnPh_3$ (**I**)
$(L^2)SnPh_3$ (**II**)
$(L^3)SnPh_3$ (**III**)
$(L^4)SnPh_3$ (**IV**)
$(L^5)SnPh_3$ (**V**)

Scheme 2.

Complexes **I**–**V** in the solid state are finely crystalline yellow or orange powders. Their solutions are colored in dark yellow (**I**–**III**) or orange-red (**IV**, **V**). Unlike compounds **I**–**III**, compounds **IV** and **V** are insoluble in toluene, diethyl ether, acetonitrile, and hexane. The synthesized complexes in the solid state are rather resistant to air oxygen and moisture.

Compounds **I**–**V** were studied by IR and ^{1}H NMR spectroscopy. The molecular structures of

Table 1. Crystallographic data and experimental and structure refinement parameters for compounds **II** and **III**

Parameter	Value	
	II	**III**
Composition	$C_{32}H_{27}NOSn$	$C_{31}H_{24}ClNOSn$
FW	560.23	580.65
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
T, K	298	100
λ, Å	0.71073 (Mo)	0.71073 (Mo)
a, Å	9.0356(2)	8.9326(8)
b, Å	9.6545(3)	9.5885(8)
c, Å	16.3057(5)	15.8917(13)
α, deg	72.928(3)	73.198(2)
β, deg	84.124(2)	82.224(2)
γ, deg	85.335(2)	85.600(2)
V, Å^3	1350.63(7)	1290.02(19)
Z	2	2
ρ_{calc}, g/cm^3	1.378	1.495
μ, mm^{-1}	0.969	1.118
F(000)	568	584
Crystal sizes, mm	0.28 × 0.21 × 0.18	0.33 × 0.17 × 0.12
Scan range over θ, deg	3.08–28.70	2.53–30.11
Number of measured/independent reflections	31 183/6959	18 289/7568
R_{int}	0.0322	0.0335
Number of independent reflections with $I > 2\sigma(I)$	5979	6611
Number of refined parameters/restraints	317/0	316/0
R ($F^2 > 2\sigma(F^2)$)	$R_1 = 0.0309$, $wR_2 = 0.0715$	$R_1 = 0.0368$, $wR_2 = 0.0777$
R (for all data)	$R_1 = 0.0401$, $wR_2 = 0.0752$	$R_1 = 0.0466$, $wR_2 = 0.0808$
$S(F^2)$	1.040	1.057
Residual electron density (max/min), e/Å^3	0.65/–0.33	2.10/–1.34

complexes **II** and **III** in the crystalline state were determined by XRD.

The IR spectra of the tin(IV) phenolate complexes contain a set of characteristic bands corresponding to stretching vibrations of the ordinary C–O bonds of the phenol fragment in a range of 1280–1220 cm^{-1}. Similarly to the starting *o*-iminophenolate ligands, stretching vibrations of the –C=N– bond appear as medium- and strong-intensity bands at 1640–1570 cm^{-1}.

The ^{1}H NMR spectra of the complexes contain signals from protons of the groups (aromatic, phenyl, and

Table 2. Selected bond lengths (Å) and angles (deg) in $(L^2)SnPh_3$ (**II**) and $(L^3)SnPh_3$ (**III**) according to the XRD data

Bond	**II**	**III**
	d, Å	
Sn(1)–O(1)	2.0112(15)	2.0298(16)
Sn(1)–N(1)	2.781(2)	2.727(2)
Sn(1)–C(14)	2.122(2)	2.126(2)
Sn(1)–C(26)	2.127(2)	2.129(2)
Sn(1)–C(20)	2.155(2)	2.147(2)
O(1)–C(1)	1.347(2)	1.338(3)
N(1)–C(7)	1.277(3)	1.283(3)
N(1)–C(6)	1.403(3)	1.415(3)
C(1)–C(2)	1.396(3)	1.402(3)
C(1)–C(6)	1.398(3)	1.405(3)
C(2)–C(3)	1.385(3)	1.378(3)
C(3)–C(4)	1.378(4)	1.388(4)
C(4)–C(5)	1.375(4)	1.388(3)
C(5)–C(6)	1.401(3)	1.396(3)
C(7)–C(8)	1.466(3)	1.469(3)
Angle	ω, deg	
O(1)Sn(1)C(14)	114.65(8)	115.49(8)
O(1)Sn(1)C(26)	113.53(7)	114.09(8)
C(14)Sn(1)C(26)	120.42(8)	120.55(9)
O(1)Sn(1)C(20)	94.32(7)	93.65(8)
C(14)Sn(1)C(20)	104.36(8)	104.11(9)
C(26)Sn(1)C(20)	104.80(8)	103.37(9)
C(20)Sn(1)N(1)	162.17(8)	162.36(9)
O(1)Sn(1)N(1)	68.31(8)	69.00(9)

imine group) in the complexes. The protons of the imine group in the complexes appear in the ^{1}H NMR spectra as intense singlets at chemical shifts lying in a range of 8.4–8.8 ppm. The ^{119}Sn NMR spectra of complexes **I** and **II** exhibit signals at –127.4 and –132.45 ppm, respectively. It is known from published data that the tetracoordinated tin(IV) complexes are characterized by a chemical shift in the range from –40 to –120 ppm, and the shift for the pentacoordinated complexes ranges from –180 to –260 ppm. Based on the NMR spectroscopic data, the synthesized compounds in a chloroform solution can be assigned to tetracoordinated complexes, which means only a weak coordination of the imino group to the central tin atom. These observations are confirmed by the XRD data.

The molecular structures of the (5-Me(L)O)$SnPh_3$ (**II**) and (5-Cl(L)O)$SnPh_3$ (**III**) complexes in the crystalline state were determined by XRD. Selected bond lengths and angles are listed in Table 2. The molecular and crystal structures of the complexes are similar (Figs. 1, 2).

The central Sn(1) tin atom in complexes **II** and **III** exists in the distorted trigonal bipyramidal ligand environment. The base of the pyramid is formed by the C(26) and C(14) carbon atoms of two phenyl groups and O(1) oxygen atom of the *o*-iminophenolate ligand, whereas the C(20) carbon atom of the third phenyl group and N(1) nitrogen atom of the chelating ligand are arranged in the apical positions. The C–C distances of the aromatic ring C(1–6) in the *o*-iminophenolate ligand (1.375(4)–1.401(3) Å, average

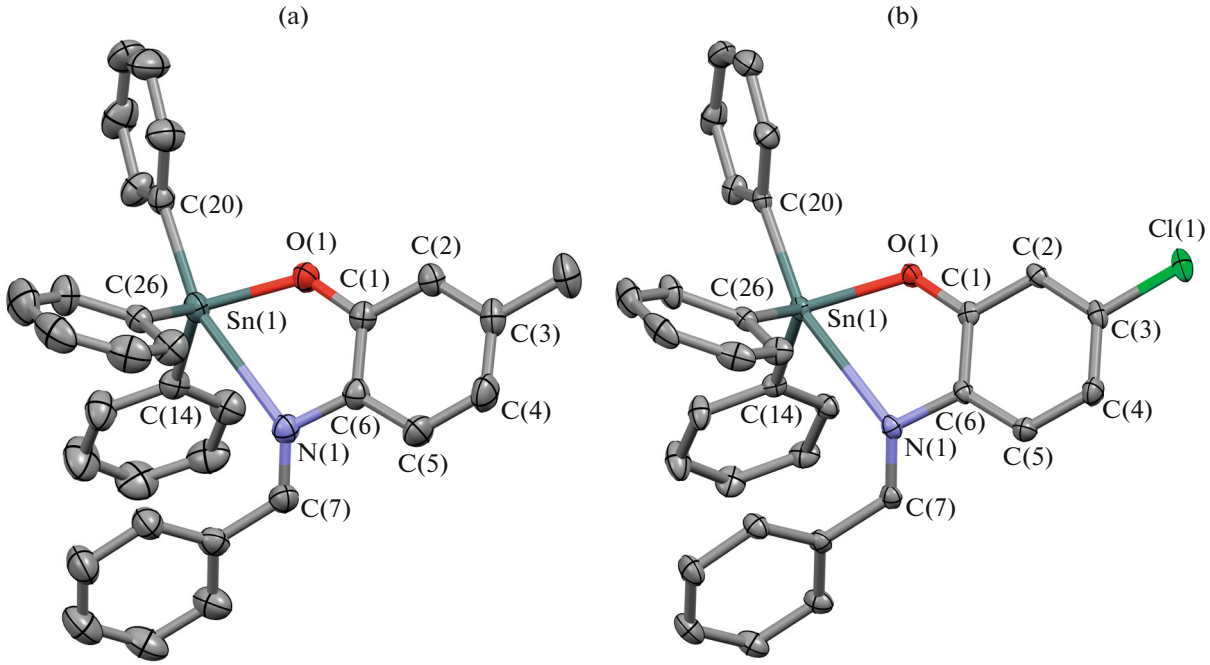


Fig. 1. Molecular structures of compounds (a) **II** and (b) **III**. Hydrogen atoms are omitted.

1.389 Å in complex **II**; 1.378(3)–1.405(3) Å, average 1.393 Å in complex **III**) are close to those in the tin *o*-iminophenolate complexes [38–40]. The C(1)–O(1) and C(6)–N(1) bond lengths (1.347(2), 1.403(3) Å in complex **II**; 1.338(3) and 1.415(3) Å in complex **III**, respectively) lie in the range of bond lengths characteristic of ordinary C–O (1.32–1.36 Å) and C–N (1.38–1.43 Å) bonds [48–57]. On the one hand, the Sn(1)–O(1) bond (2.0301(16) Å) is somewhat shorter than the sum of covalent radii of the corresponding atoms (r_{cov}(Sn) = 1.47 Å, r_{cov}(O) = 0.73 Å [58]) but is consistent with these bonds in similar *o*-iminophenolate tin complexes [38–40]. On the other hand, the Sn(1)–N(1) distances (2.781(2) Å in complex **II** and 2.727(2) Å in complex **III**) exceed the sum of covalent radii of the corresponding atoms (r_{cov}(Sn) = 1.47 Å, r_{cov}(N) = 0.74 Å [58]) but is less than the sum of the van der Waals radii (r_w(Sn) = 2.25 Å, r_w(N) = 1.6 Å [59]). The Sn(1)–N(1) distances in complexes **II** and **III** are much longer than the corresponding distances in a series of other bis-*o*-iminophenolate tin derivatives (2.1–2.3 Å [38–40]), indicating a weaker donor-acceptor Sn(1)–N(1) bond in complexes **II** and **III** compared to the earlier described *o*-iminophenolate tin(II,IV) complexes. These data are confirmed by the observations based on the ^{119}Sn NMR spectra of solutions of complexes **I** and **II**.

In crystals, the molecules of the complexes are packed in such an isolated way that pairs are formed (Fig. 2) in which the $SnPh_3$ fragments are directed to each other. The shortest distances between the carbon atoms of the phenyl rings of the adjacent $SnPh_3$ fragments in these pairs are 4.06(1) Å for complex **II** and 3.84(1) Å for complex **III**, which is larger than the sum of van der Waals radii of the carbon atoms (r_w(C) = 1.7 Å [59]).

To conclude, the series of the triphenyltin(IV) complexes with the bidentate *o*-iminophenolate ligands was synthesized. The molecular structures of two complexes (triphenyltin(IV) 2-benzylideneamino-5-methylphenolate and triphenyltin(IV) 2-benzylideneamino-5-chlorophenolate) in the crystalline state were determined by XRD.

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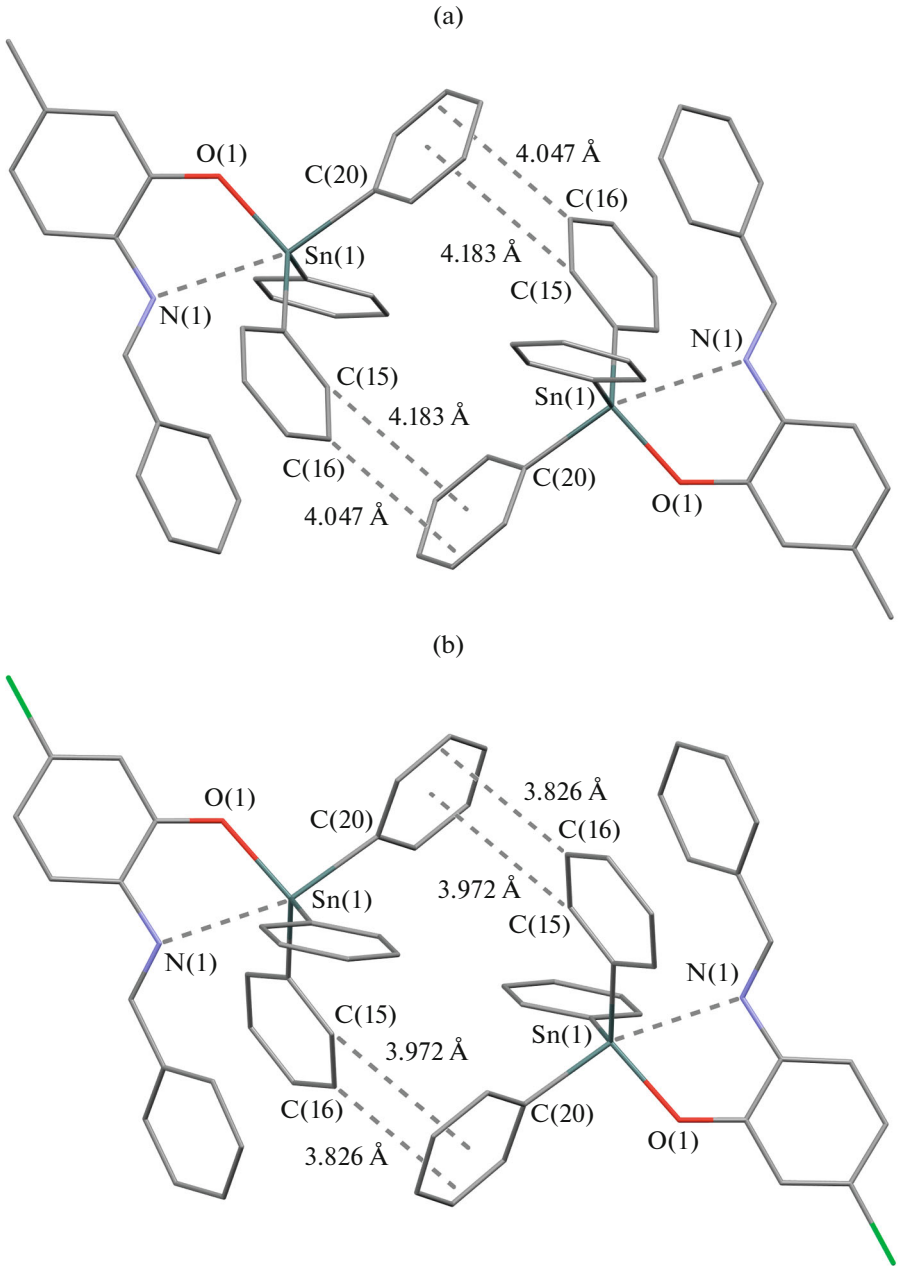

Fig. 2. Formation of pairs of molecules in the crystals of compounds (a) **II** and (b) **III**. Hydrogen atoms are omitted.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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