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New bis-o-benzosemiquinonato tin(IV) complexes

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ABSTRACT

New bis-o-benzosemiquinonato tin(IV) complexes $(3,6-SQ)_2SnCl_2$, $(3,6-SQ)_2SnBr_2$ and $(3,6-SQ)_2SnPh_2$ (3,6-SQ is radical-anion 3,6-di-*tert*-butyl-o-benzosemiquinone) were synthesized by different methods. The reaction of tin(IV) catecholates $(3,6-Cat)SnX_2\cdot 2THF$ (X = Cl, Br) with nitrogen(IV) oxide leads to EPR-active six-coordinated mono-o-benzosemiquinonato complexes of $(3,6-SQ)SnX_2(NO_2)$ -THF type which undergo symmetrization to the corresponding diradical bis-o-benzosemiquinonato species (3, $6-SQ)_2SnX_2$. Diphenyltin(IV) catecholate $(3,6-Cat)SnPh_2$ -THF reacts with Br₂, I₂ and NO₂ to give five-coordinated species $(3,6-SQ)SnPh_2X$ (X = Br, I, NO₂) which transform to bis-(o-benzosemiquinonato)diphenyltin(IV) $(3,6-SQ)_2SnPh_2$. The molecular structures of $(3,6-SQ)_2SnBr_2$ and $(3,6-SQ)_2SnPh_2$ were determined by X-ray analysis.

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1. Introduction

The coordination chemistry of tin(IV) complexes containing redox-active *o*-quinonato ligands is rapidly developing [1]. Despite this, there are only two examples of bis-*o*-semiquinonato tin(IV) complexes which have been isolated and characterized by physicochemical methods [2]. Some techniques to synthesize tin(IV) complexes, based on *o*-quinonato ligands, such as interaction of tin salts with *o*-quinones and *o*-semiquinonato alkali metal or thallium derivatives, as well as fixation of small molecules, for example halogens, by catecholate tin(IV) complexes are well known at present [3]. However, neither of these methods, nor a new method – disproportionation – has been exploited to synthesize tin(IV) bis*o*-semiquinolates. In this paper, we report the synthesis of new bis-*o*-benzosemiquinonato tin(IV) complexes, along with physicochemical and EPR investigations of these compounds.

2. Experimental

Infrared spectra of complexes were recorded in the 400– 3500 cm⁻¹ range on a FSM-1201 spectrophotometer in Nujol mulls and reported in cm⁻¹. X-band EPR spectra were recorded on Bruker EMX (working frequency ~9.7 GHz) spectrometer. The g_i values were determined using DPPH as the reference ($g_i = 2.0037$). HFC constants were obtained by simulation with the WINEPR SIMFONIA Software (Bruker).

X-ray diffraction data for 8 and 13 were collected using Oxford Diffraction (Gemini S) diffractometer with graphite monochromated Mo-K α radiation (μ = 0.71073 Å) and with CCD detector Sapphire III in the ω -scan mode. X-ray data on samples 8 and 13 were collected at temperature 100 K. The crystal structure was solved by direct methods (SHELX97) [4] and refined by full matrix method (WINGX and SHELX97) [5]. The reflection data were processed using the analytical absorption correction algorithm [6]. All nonhydrogen atoms were refined with anisotropic correction. All H atoms were placed in calculated positions and refined in the "riding-model" $(U_{iso}(H) = 1.2 \cdot U_{eq}(\text{carbon}) \text{ A}^2 \text{ for aromatic hydrogen}$ and 1.5 U_{eq} (carbon) A² for alkyl hydrogen). The follow minimal R_1 -factors obtained for **8** and **13** correspond to $R_1 = 0.0346$ and 0.0399, respectively. The selected bond distances and angles for 8 and 13 are given in Table 1. Table 2 summarizes the crystal data and some details of the data collection and refinement.

The 3,6-di-*tert*-butyl-o-benzoquinone was obtained using method described in [7a]. Other starting reagents were purchased in Aldrich. Solvents were purified following standard procedures [7b]. All manipulations on complexes were performed under conditions excluding air oxygen and moisture. (3,6-Di-*tert*-butyl-o-benzosemiquinonato)tallium(I) ((3,6-SQ)Tl, **1**) [8], bis-(3, 6-di-*tert*-butylcatecholato) tin(IV) ditetrahydrofuranate ((3,6-Cat)₂Sn·2THF, **2**) [1c], (3,6-di-*tert*-butylcatecholato)dichlorotin(IV)



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Table 1								
Selected	bonds a	and an	gles in	com	plexes	8	and	13.

Bond, Å	(3,6-SQ) ₂ SnBr ₂	(3,6-SQ) ₂ SnPh ₂
Sn(1)-O(1)	2.0804(13)	2.124(2)
Sn(1)-O(2)	2.1080(14)	2.217(2)
Sn(1)-O(3)	2.0805(13)	2.111(2)
Sn(1)-O(4)	2.1080(14)	2.188(2)
O(1)-C(1)	1.298(2)	1.295(3)
O(2)-C(2)	1.293(2)	1.260(4)
O(3)-C(7)	1.298(2)	1.301(4)
O(4) - C(8)	1.293(2)	1.283(4)
C(1)-C(2)	1.470(3)	1.485(4)
C(1)-C(6)	1.427(3)	1.412(4)
C(2)-C(3)	1.415(3)	1.453(4)
C(3)-C(4)	1.363(3)	1.337(5)
C(4) - C(5)	1.424(3)	1.433(5)
C(5)-C(6)	1.365(3)	1.372(4)
C(7) - C(8)	1.470(3)	1.469(4)
C(7)-C(12)	1.427(3)	1.418(4)
C(8) - C(9)	1.415(3)	1.441(4)
C(9)-C(10)	1.363(3)	1.359(5)
C(10)-C(11)	1.424(3)	1.416(5)
C(11)-C(12)	1.365(3)	1.371(5)
Sn(1)-Br(1)	2.4902(3)	
Sn(1)-Br(2)	2.4902(3)	
Sn(1)-C(13)		2.155(3)
Sn(1)-C(14)		2.146(3)
Angle		
O(1) - Sn(1) - O(2)	77.21(5)	75.07(8)
O(1)-Sn(1)-O(3)	153.93(8)	151.34(8)
O(1) - Sn(1) - O(4)	83.39(5)	83.53(8)
O(2) - Sn(1) - O(4)	83.50(8)	76.66(8)
O(2) - Sn(1) - O(3)	83.39(5)	82.19(8)
O(3) - Sn(1) - O(4)	77.21(5)	74.31(8)
O(1) - Sn(1) - Br(1)	93.22(4)	
O(1) - Sn(1) - Br(2)	103.50(4)	
O(2)-Sn(1)-Br(1)	168.31(4)	
O(2)-Sn(1)-Br(2)	88.79(4)	
O(3) - Sn(1) - Br(1)	103.50(4)	
O(3) - Sn(1) - Br(2)	93.22(4)	
O(4)-Sn(1)-Br(1)	88.79(4)	
O(4)-Sn(1)-Br(2)	168.31(4)	
Br(1) - Sn(1) - Br(2)	100.100(13)	
O(1)-Sn(1)-C(13)		92.77(10)
O(1) - Sn(1) - C(14)		103.52(10)
U(2) - Sn(1) - U(13)		162.48(10)
U(2) - Sn(1) - C(14)		88.47(10)
O(3) - Sn(1) - C(13)		104.33(10)
O(3) - Sn(1) - C(14)		93.66(10)
O(4) - Sn(1) - C(13)		90.10(10)
O(4) - Sn(1) - C(14)		162.13(10)
C(13) - Sn(1) - C(14)		106.33(12)

ditetrahydrofuranate ((3,6-Cat)SnCl₂·2THF, **3**) [3c], (3,6-di-*tert*-butylcatecholato)dibromotin(IV) ditetrahydrofuranate ((3,6-Cat)SnBr₂·2THF, **4**) [3d], (3,6-di-*tert*-butylcatecholato)diphenyl-tin(IV) tetrahydrofuranate ((3,6-Cat)SnPh₂·THF, **9**) [3b] were synthesized according to literature procedures.

2.1. Bis-(3,6-di-tert-butyl-o-benzosemiquinonato)tin(IV) dichloride, (3,6-SQ)₂SnCl₂ (7)

Method I, Scheme 1: $SnCl_4$ (2.5 mmol, 0.29 ml) was added to the solution of complex **1** (5 mmol, 2.13 g) in 50 ml of toluene. The white residue of TlCl precipitated from reaction mixture. The dark-green solution of complex **7** was filtered using glass Shott filter No. 4. The dark-green fine-crystalline powder of complex **7** (1.23 g, yield is 78.4%) was obtained by recrystallization from toluene–hexane mixture.

Method III, Scheme 1: The solution of SnCl₂-diox (1 mmol, 0.277 g) in 10 ml of acetonitrile was drop added to the solution

of 3,6-di-*tert*-butyl-o-benzoquinone (2 mmol, 0.440 g) in 20 ml of the same solvent. The color of reaction mixture turned from green–red to dark-green. The dark-green residue of complex **7** (0.480 g, yield is 76%) precipitated from reaction mixture after some minutes.

Method IV, Scheme 1: The one equivalent of gaseous NO₂ (1 mmol, 0.046 g) was added to the solution of complex **3** (1 mmol, 0.554 g) in the mixture of 10 ml of acetonitrile and 10 ml of toluene. The dark-green crystals of complex **7** (0.205 g, yield is 65%) was obtained after 12 h storage at -12 °C.

Anal. Calc. for C₂₈H₄₀Cl₂O₄Sn,%: C, 53.36; H, 6.40; Cl, 11.25; Sn, 18.84. Found: C, 53.41; H, 6.37; Cl, 11.28; Sn, 18.93.

IR (nujol, cm⁻¹): 1482 s., 1437 s., 1416 s., 1392 m., 1366 s., 1351 w., 1332 w., 1281 m., 1208 m., 1183 w., 1027 w., 970 m., 954 s., 931 w., 850 w., 842 w., 806 w., 685 s., 652 m., 581 m., 494 m.

2.2. Bis-(3,6-di-tert-butyl-o-benzosemiquinonato)tin(IV) dibromide, (3,6-SQ)₂SnBr₂ (8)

Method II, Scheme 1: The solution of Br_2 ·diox (1 mmol, 0.248 g) in 10 ml of THF was drop added to the solution of **2** (1 mmol, 0.559 g) in 20 ml of THF. The color of reaction mixture changed from yellow to dark-green). The solvent was evaporated and the residue was dissolved in 15 ml of toluene. The dark-green crystals of **8** (0.575 g, yield is 80%) were isolated from this solution after 12 h storage at -12 °C.

Method III, Scheme 1: The solution of SnBr_2 ·diox (1 mmol, 0.367 g) in 10 ml of acetonitrile was drop added to the solution of 3,6-di-*tert*-butyl-o-benzoquinone (2 mmol, 0.440 g) in 20 ml of the same solvent. The color of reaction mixture turned from green–red to dark-green. The dark-green residue of complex **8** (0.582 g, yield is 81%) precipitated from reaction mixture after some minutes.

Method IV, Scheme 1: The one equivalent of gaseous NO₂ (1 mmol, 0.046 g) was added to the solution of complex **4** (1 mmol, 0.643 g) in the mixture of 10 ml of acetonitrile and 10 ml of toluene. The dark-green crystals of complex **8** (0.244 g, yield is 68%) suitable for X-ray analysis were obtained after 12 h storage at -12 °C.

Anal. Calc. for C₂₈H₄₀Br₂O₄Sn,%: C, 46.76; H, 5.61; Br, 22.22; Sn, 16.51. Found: C, 46.71; H, 5.65; Br, 22.15; Sn, 16.48.

IR (nujol, cm⁻¹): 1484 s., 1415 s., 1391 s., 1370 m., 1360 s., 1351 w., 1334 m., 1289 w., 1276 m., 1208 m., 1183 w., 1029 w., 968 s., 956 s., 932 w., 836 s., 807 m., 686 s., 651 s., 578 m., 494 s.

2.3. Bis-(3,6-di-tert-butyl-o-benzosemiquinonato)diphenyl tin(IV), (3,6-SQ)₂SnPh₂ (13)

Method I, Scheme 2: The one equivalent of gaseous NO_2 (1 mmol, 0.046 g) was added to the solution of complex **9** (1 mmol, 0.565 g) in 20 ml of acetonitrile. The dark-violet residue of complex **13** (0.271 g, yield is 76%) precipitated from reaction mixture immediately. The suitable crystals for X-ray analysis were obtained after prolonged crystallization from the mixture of toluene and acetonitrile.

Method II, Scheme 2: The solution of $Br_2 \cdot diox$ (0.5 mmol, 0.124 g) in 10 ml of acetonitrile was drop added to the solution of complex **9** (1 mmol, 0.565 g) in 20 ml of the same solution. The dark-violet residue of complex **13** (0.253 g, yield is 71%) precipitated from reaction mixture immediately.

Method III, Scheme 2: The solution of I_2 (1 mmol, 0.254 g) in 10 ml acetonitrile was drop added to the solution of complex **9** (1 mmol, 0.565 g) in 20 ml of the same solvent. The dark-violet residue of complex **13** (0.267 g, yield is 75%) precipitated from reaction mixture immediately.

Anal. Calc. for $C_{40}H_{50}O_4Sn$,%: C, 67.33; H, 7.06; Sn, 16.64. Found: C, 67.21; H, 7.12; Sn 16.71.

Formula	$C_{28}H_{40}Br_2O_4Sn$	C ₄₀ H ₅₀ O ₄ Sn
M	719.11	713.49
T (K)	100 (2)	100 (2)
Crystal system	Monoclinic	Monoclinic
Space group	C 1 2/c 1	C 1 2/c 1
Unit cell dimensions	16.7018 (5)	35.1558 (8)
a (Å)	12.8969 (3)	10.2093 (2)
b (Å)	15.7698 (4)	20.6444 (5)
c (Å)	90	90
α (°)	111.628 (3)	96.520 (2)
β (°)	90	90
γ (°)	3157.69 (15)	7361.7 (3)
V (Å ³)	4	8
Z	1440	2976
F (000)	1.513	1.288
Calculated density, (mg/m ³)	3.368	0.731
Absorption coefficient, (mm ⁻¹)	$3.44 \le \theta \le 32.91$	$3.43 \le \theta \le 23.26$
θ (°)	$-23 \le h \le 23$	$-28 \le h \le 38$
Limiting indices	$-10 \le k \le 18$	$-11 \le k \le 11$
Maximum and minimum transmission Reflections collected Independent reflections (R_{int}) Absorption correction Refinement method Data/restraints/parameters Final R indices [$I > 2\sigma(I)$] R indices (all data) Goodness-of-fit (GOF) on (F^2) $\Delta \rho_{max} \Delta \rho_{min}$, ($e \ Å^{-3}$)	$-21 \le l \le 22$ 1 and 0. 88993 4767 3148 (0.0324) Multi-scan Full-matrix least-squares on F^2 3148/0/159 $R_1 = 0.0346$, $wR_2 = 0.0668$ $R_1 = 0.0585$, $wR_2 = 0.069$ 0.849 1.748/-0.711	$-21 \le l \le 22$ 0.948 and 0.872 5264 3817 (0.0411) Analytical Full-matrix least-squares on F^2 3817/0/406 $R_1 = 0.0399, wR_2 = 0.0768$ $R_1 = 0.0604, wR_2 = 0.0798$ 0.997 2.549/-0.611

Table 2Summary of crystal and refinement data for complexes 8 and 13.

IR (nujol, cm⁻¹): 1578 w., 1548 w., 1493 m., 1428 s., 1356 m., 1338 m., 1277 w., 1201 w., 1182 w., 1154 w., 1074 w., 1059 w., 1024 w., 997 w., 967 m., 955 s., 930 w., 834 m., 807 w., 697 s., 679 m., 652 m., 552 m., 496 m.

3. Results and discussion

The main methods of synthesis of nontransition metal *o*-semiquinonato complexes consist in the interaction of low valence metal salts or metal amalgams with *o*-quinones, the addition of the different species to catecholate nontransition metal complexes and the exchange interaction of *o*-semiquinonato alkali metal or thallium complexes with nontransition metal salts [3a].

For the preparation of o-quinonato nontransition metal complexes, the solution medium plays an important role [2b,3c,9]. As shown in work [3c] the addition of 3,6-di-tert-butyl-o-benzoquinone to SnCl₂ in THF solution leads to the oxidation of Sn(II) to Sn(IV), the reduction of o-quinone to catecholate dianion and the formation of catecholate complex (3,6-Cat)SnCl₂·2THF (**3**). The complex 3 is generated independently of the molar ratio of 3,6di-tert-butyl-o-quinone to tin (1:1 or 2:1). This fact can be explained by the high coordination ability of THF towards tin as shown in work [10]. The formation of catecholate tin(IV) complex stabilized by two THF molecules is more thermodynamically advantageous than the replacement of coordinated THF in complex **3** by 3,6-di-*tert*-butyl-o-benzoquinone followed by the intramolecular redox process between redox-active ligands. However the change of THF with acetonitrile as weaker base [11] allows to obtain diradical tin(IV) complex 7 (Scheme 1, method III). Worthy of note that the dissolution of diradical complex $(3,6-SQ)_2SnCl_2(7)$ or its dibromine analogue $(3,6-SQ)_2SnBr_2$ (8) and their storage in THF leads to the elimination of 3,6-di-tert-butyl-o-benzoquinone and the formation of corresponding monocatecholates (3,6-Cat)SnCl₂₋ ·2THF (**3**) or (3,6-Cat)SnBr₂·2THF (**4**).

The interaction of *o*-semiquinonato alkali metal or thallium derivatives with nontransition metal salts is one of the widely used synthetic methods to *o*-semiquinonato metal complexes [3a,12]. As shown in present work, the exchange interaction of 3,6-di-*tert*-butyl-*o*-benzosemiquinonato tallium(I) and SnCl₄ in toluene solution in the molar ratio 2:1 (Scheme 1, method I) leads to the formation of bis(3,6-di-*tert*-butyl-*o*-benzosemiquinona-to)tin(IV) dichloride (**7**).

As shown earlier, the fixation of O-, N-, S-centered free radicals and other species, for example halogens, by catecholate non-transition metal complexes is attended by one-electron oxidation of the catecholate dianion to the *o*-semiquinonato radical-anion [3]. As reported in [3d] the addition of halogens to the catecholate tin(IV) complexes **3** and **4** yields the monoradical (3,6-di-*tert*-butyl-*o*-benzosemiquinonato)trihalogenotin(IV) complexes. The interaction of nitrogen dioxide NO₂ with **3** and **4** gives firstly 3,6di-*tert*-butyl-*o*-benzosemiquinonato tin(IV) species **5** and **6** with the appearance of EPR activity (see Section 3.2), however at the next stage the symmetrization of these complexes to the diradical derivatives **7** and **8** takes place (Scheme 1, method IV). The oxidative addition of Br₂ to bis-catecholate **2** in equimolecular ratio also leads to diradical complex **8** (Scheme 1, method II).

The oxidative addition of halogens and NO₂ to (3,6-di-tert-butyl-catecholato)diphenyltin(IV) tetrahydrofuranate (**9**) resulting at the first stage in formation of monoradical species **10–12** which are characterized by EPR (see Section 3.2, Table 3), leads to the symmetrization of these monoradical species to the stable diradical complex **13** (Scheme 2, methods I–III).

It should be noted that authors [13] supposed that the product of exchange interaction between Ph_2SnCl_2 and (3,5-SQ)Na (molar ratio 1:2) in *n*-hexane-dichloromethane mixture – bis-(3,5-di*tert*-butyl-*o*-benzosemiquinonato)diphenyltin(IV) – is unstable and undergoes intermolecular electron-transfer process with formation of catecholate tin(IV) complex and free neutral 3,5-di-





tert-butyl-o-benzoquinone. The present results demonstrate that bis-o-benzosemiquinonato tin(IV) complexes $(SQ)_2SnX_2$ are stable compounds and can be isolated without decomposition under certain conditions.

Complexes were characterized by IR, EPR spectroscopy and elemental analysis. The typical vibration bands in 1460–1350 cm⁻¹ range in IR-spectra corresponding to C<u>-</u>O one-and-half bonds confirm the radical-anion nature of complexes **7**, **8** and **13**.

Table 3	
EPR spectral parameters on	complexes 5 , 6 and 10–12 .

Complex	g _i	<i>a_i</i> (¹ H), G	<i>a</i> _{<i>i</i>} (¹¹⁷ Sn)/ <i>a</i> _{<i>i</i>} (¹¹⁹ Sn), G	a _i (Hal), G
5	2.0033	2 ¹ H 3.86	7.31/7.65	³⁵ Cl/ ³⁷ Cl 0.6/0.5
10	2.0038	¹ H 2.96	4.95/5.18 16.25/17.0	DI/ DI 2.20/2.44
11	2.0038	¹ H 4.7 ¹ H 2.81	15.97/16.7	
12	2.004	¹ H 4.71 ¹ H 2.88 ¹ H 4.72	15.53/16.24	

Toluene, RT.

3.1. Structural studies

The X-ray suitable crystals of 8 and 13 were obtained by the prolonged crystallization from the mixture of toluene and acetonitrile. Fig. 1 shows the molecular structures of 8 and 13. The selected bond lengths and angles are listed in Table 1. The tin(IV) atom in both complexes has the distorted octahedral environment formed by two o-benzosemiquinonato ligands and two bromine atoms (complex 8) or two carbon atoms of phenyl groups (complex 13). The geometrical features of chelating ligands confirm their radical-anion forms. The O-C distances in both o-benzosemiquinonato ligands of complexes 8 and 13 lie in the range of 1.293-1.301 Å and correspond the one-and-half O–C distances in such type ligands [3d,9,14] but shorter than in catecholate dianion ligands (1.33–1.39 Å) [3b,3c,14a,15]. The six-membered carbon rings of chelating ligands demonstrate the quinoid-type distortion expressing by nonequivalence of C-C distances. Both complexes adopt cis-configuration and the angle between chelating ligands planes is 76.45° in 8 and 73.27° in 13. The trans effect of bromine and phenyl ligands in complexes 8 and 13 is reflected in the elongation of the corresponding Sn-O bonds (Sn(1)-O(2)) and Sn(1)-O(2)O(4)) and the shortening of the corresponding O-C bonds of SO ligands (O(2)-C(2) and O(4)-C(8)) (Table 1).

3.2. EPR studies

The addition of NO₂ to **3**, **4** and **9** and Br₂ and I₂ to **9** leads firstly to the formation of paramagnetic mono-*o*-benzosemiquinonato complexes **5**, **6** and **10–12**, respectively. The EPR spectral parameters on complexes are collected in Table 3. Figs. 2 and 3 show the X-band EPR spectra of complexes **5** and **11**, respectively.



Fig. 2. Experimental X-band EPR spectrum of complex **5** (RT, toluene) and its computer simulation (WINEPR SIMFONIA Software).

The hyperfine structure (HFS) of EPR spectra of these complexes is caused by hyperfine coupling (HFC) of unpaired electron with two equivalent protons (¹H, 99.98%, *I* = 1/2, $\mu_{\rm N}$ = 2.7928 [16]) (4th and 5th positions of aromatic ring of 3,6-SQ ligand) and halogen atom in apical position (³⁵Cl, 75.77%, *I* = 3/2, $\mu_{\rm N}$ = 0.82187, ³⁷Cl, 24.23%, *I* = 3/2, $\mu_{\rm N}$ = 0.68412; ⁷⁹Br, 50.69%, *I* = 3/2, $\mu_{\rm N}$ = 2.1064, ⁸¹Br, 49.31%, *I* = 3/2, $\mu_{\rm N}$ = 2.2706 [16]) in case of six-coordinated complexes **5**–**6** and with two nonequivalent protons in case of five-coordinated complexes **10–12**. The satellite splitting on ¹¹⁷Sn and ¹¹⁹Sn magnetic isotopes (¹¹⁷Sn, 7.68%, *I* = 1/2, $\mu_{\rm N}$ = –1.000, ¹¹⁹Sn, 8.58%, *I* = 1/2, $\mu_{\rm N}$ = –1.046 [16]) also takes place in all EPR spectra of obtained *o*-benzosemiquinonato derivatives (Figs. 2 and 3).

According to EPR data, complexes **5** and **6** are six-coordinated and have the octahedral environment with the first halogen atom and oxygen atom of THF molecule in the apical positions and



Fig. 1. The molecular structures of complexes 8 (left) and 13 (right) with ellipsoids of 30% probability. The hydrogen atoms are omitted for clarity.



Fig. 3. Experimental X-band EPR spectrum of complex **11** (RT, toluene) and its computer simulation (WINEPR SIMFONIA Software).

oxygen atoms of *o*-benzosemiquinonato ligand, the second halogen atom and NO₂-group in the basal plane. Complexes **10–12** are fivecoordinated and have a square-pyramidal geometry with phenyl group in the apical position and oxygen atoms of *o*-semiquinonato ligand, other phenyl group and substituent Y (NO₂, Br, I) in the basal plane. The unsymmetrical position of substituents at tin atom relative to the plane of SQ ligand reflects in the unequivalence of protons in 4th and 5th positions of SQ ligand (Table 3). The values of ¹¹⁷Sn and ¹¹⁹Sn HFC constants for complexes **5–6** are typical for six-coordinated *o*-semiquinonato tin(IV) complexes while for **10–12** are typical for five-coordinated *o*-semiquinonato tin(IV) complexes (4–7 G for six-coordinated and 9–20 G for fivecoordinated complexes [3,1a,1b,17]).

Bis-o-benzosemiquinonato complexes **7**, **8** and **13** are characterized by EPR signals in normal and half-field ($\Delta m_s = 2$) at low temperature in the glass solvent matrix, typical for diradical species with *S* = 1 (Fig. 4). The zero-splitting parameters D and E of complexes are the following: 268 G and 61 G for **7**, 340 G and 60 G for **8**, 325 G and 42 G for **13**. The average distances *r* between radical centers calculated from *D* using the approximation of dot dipoles [18] ($r = (55600/2D)^{1/3}$) are the following: 4.7 Å for **7**,



Fig. 4. The anisotropic X-band EPR spectrum of complex **13** (150 K, toluene). Parameters $D_{II} = 650$ G, E = 42 G. The transition $\Delta m_s = 2$ is shown in the insertion.

4.3 Å for **8** and 4.4 Å for **13**. These values are very close to the distances between the centroids of the bands C–C of SQ chelating rings (4.25 Å in **8** and 4.28 Å in **13**).

4. Conclusions

New bis-o-benzosemiquinonato tin(IV) complexes $(3,6-SQ)_2SnX_2$ (X = Cl, Br, Ph) were synthesized by different methods such as the substitution reaction between tin(IV) halide and alkali metal o-semiquinolate (1:2); the oxidative addition of o-quinone to SnX_2 in acetonitrile; oxidation of bis-catecholato tin(IV) with bromine. It is important to note that, in some methods, the solvent nature plays a crucial role: the target synthesis of tin(IV) bis-o-benzosemiquinolates SQ_2SnX_2 proposes the use of acetonitrile instead of THF which is common solvent in syntheses of tin(IV) catecholates.

The reaction of tin(IV) monocatecholates $(3,6-Cat)SnX_2 \cdot nTHF$ (X = Cl, Br, n = 2; X = Ph, n = 1) with NO₂ proceeds through the formation of monoradical five- or six-coordinated *o*-semiquinonato species which undergo symmetrization to the corresponding diradical complexes $(3,6-SQ)_2SnX_2$. The same transformations take place in the case of mono-*o*-semiquinonato-diphenyltin(IV) complexes with halides $(3,6-SQ)SnPh_2X$ (X = Br, I) and lead to $(3,6-SQ)_2SnPh_2$.

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Appendix A. Supplementary material

CCDC 863613 and 863612 contain the supplementary crystallographic data for compounds **8** and **13**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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