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LETTERS TO THE EDITOR

3,6-Di-*tert*-butylcatecholates of Triaryl Antimony(V): NMR Study and Redox-Transformations

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Recently the ability of complexes of non-transition metals to reversibly add molecular oxygen was found by the example of *o*-amidophenolate and catecholate (Cat) complexes of triphenyl antimony(V) with donor methoxy groups in the 4 and 5 positions of the aromatic ring of the catecholate ligand [1, 2]. Variation in the nature of the substituents in the Cat ligand affects the reactivity of these compounds with respect to oxygen: The introduction of electron-withdrawing groups results in the formation of the air-stable catecholate s, whereas the presence of electron-donor groups makes it possible for these complexes to add molecular oxygen [3–7]. The investigation of electrochemical properties of the complexes has shown that the acceptor groups in the Cat ligand shift the oxidation potential of the catecholate to electropositive region (hamper the anodic process) and decrease the stability of the cationic complexes; the donor substituents, vice versa, facilitate oxidation of the Cat ligand with molecular oxygen (shift the oxidation potential to the cathode field), favoring interaction with oxygen. However, at present there are no data in the literature on the effect of the redox-inert organic fragments at the antimony atom on redox-transformations of the Cat ligand in complexes of the formula $(Cat)SbAr_3$.

In order to study the effect of the nature of the aryl substituents at the central antimony atom on the redox properties of the catecholate ligand we have synthesized complexes of tris-*p*-tolyl antimony (3,6-Cat)·$Sb(p\text{-}Tol)_3$ (**I**), triphenyl antimony $(3,6\text{-}Cat)Sb(Ph)_3$ (**II**), tris-*p*-fluorophenyl antimony $(3,6\text{-}Cat)Sb(p\text{-}F\text{-}Ph)_3$ (**III**) by the reaction of oxidative addition of 3,6-di-*tert*-butyl-*o*-benzoquinone (3,6-Q) to the corresponding stibines:

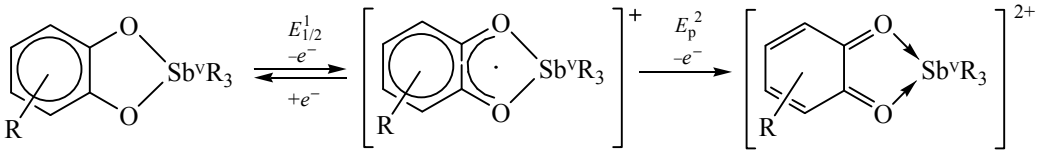
$$3,6\text{-}Q + SbAr_3 \rightarrow (3,6\text{-}Cat)SbAr_3.$$

The products were characterized by IR and ^1H and ^{13}C NMR spectroscopy. Complex of triphenyl antimony **II** was described earlier [3], but the ^{13}C NMR data for it are given in the present work for the first time. For the studied antimony(V) complexes, we have found a correlation between the ^1H and ^{13}C chemical shifts of protons and the carbon atoms in the aromatic rings in the NMR spectra as well as with oxidation potentials of the 3,6-Cat ligand.

On going from compound **I** with electron-donor methyl groups to the unsubstituted complex **II** and further to **III**, which contains the fluorine atoms in the para-position of the phenyl ring, the chemical shift of protons in the 4 and 5 positions of the Cat ligand changes from 6.59 to 6.63 ppm. Even more notable changes on going from **I** to **III** are observed in the ^{13}C NMR spectra: for carbon atoms attached to the oxygen atoms $\Delta\delta$ = 0.86 ppm, for carbon atoms attached to *tert*-butyl groups, $-\Delta\delta$ = 0.31 ppm, and for carbon atoms in the 4 and 5 positions of the Cat ligand – $\Delta\delta$ = 0.67 ppm.

According to the data of cyclic voltammetry (CVA) for the studied compounds, the first stage of oxidation is quasi-reversible one-electron process leading to the formation of relatively stable radical-anion forms of

the coordinated chelate-bonded ligand. The extention of the potential sweep range to the anodic region allows the detection of the second slightly reversible oxidation peak corresponding to the *o*-semiquinone → *o*-benzoquinone transition with the formation of dicationic complex:



According to the electronic effects of the substituents in the aromatic fragments, the values of the first half wave oxidation potentials can be arranged in the following order (see the table):

(3,6-DBCat)Sb(*p*-F-Ph)$_3$ < (3,6-DBCat)Ph$_3$Sb < (3,6-DBCat)Sb(*p*-Tol)$_3$

The data obtained in acetonitrile differ from those obtained in dichloromethane (see the table). The coordinating effect of the solvent can be seen from the $E^1_{1/2}$ values, which are shifted to the cathode region. It should be noted that the effect of the substituents on the potential of the first anodic stage is preserved also in acetonitrile; the difference between the values of the potentials of the second anodic stages for (3,6-DBCat)·Sb(*p*-F-Ph)$_3$ and (3,6-DBCat)Ph$_3$Sb is expressed more explicitly.

The comparison of the ^{13}C NMR spectroscopy data, first half-wave oxidation potentials $E^1_{1/2}$, and the Hammett constants of the substituents has shown that there is a linear correlation between the value of the average chemical shift of the carbon atoms of the aromatic ring of the catecholate ligand (see the table) with the potentials of the first redox-transition with the correlation coefficient of 0.9966, and with the values of the Hammett constants of the substituents σ_p (F = 0.06; H = 0; Me = –0.17) with the correlation coefficient of 0.9966 [8].

The data obtained are indicative of existence of electronic interaction between the two organic fragments of the molecule separated by the atom of the non-transition element. The observed correlations permit a prediction of the redox properties of new catecholate complexes of triaryl antimony(V) and the development of the strategy of synthesis of antimony compounds capable of binding molecular oxygen.

Complexes **I–III** were obtained by mixing the solutions of 1 mmol of 3,6-di-*tert*-butyl-*o*-benzoquinone and 1 mmol of the corresponding triaryl antimony in toluene (~30 ml). After the reagents were mixed and the solution turned yellow-orange, the solvent was replaced by hexane (~30 ml) and the solution obtained was allowed to stay overnight at ~0ºC. The formed yellow fine-crystalline precipitates were washed with cold hexane and dried in a vacuum. In all cases the yield was >90%.

(3,6-Cat)Sb(*p*-Tol)$_3$ (I). IR spectrum, ν, cm^{-1}: 1592 m, 1488 m, 1401 s, 1352 m, 1309 m, 1283 w, 1265 m, 1240 s, 1205 w, 1187 s, 1145 m, 1070 m, 1063 m, 1027 w, 1016 w, 977 s, 941 m, 925 w, 810 w, 798 s, 793 s, 694 s, 645 m, 607 m, 580 m, 554 w, 484 s,

Mean values of the chemical shift δ_m of the aromatic ring carbon atoms of the Cat ligand in the ^{13}C NMR spectra, oxidation potentials of the catecholate complexes of triphenyl antimony(V) from the CVA method[a]

Comp. no.	σ_p	δ_m, ppm	$E^1_{1/2}$, V	I_c/I_a	n	E^2_p, V	I_c/I_a
			(CH_2Cl_2/CH_3CN)				
I	–0.17	130.48	0.838/0.754	0.82/0.54	1.0	1.345[b]/1.261[c]	0.40/–
II	0	130.56	0.888/0.773	0.82/0.52	1.0	1.400[b]/1.293[c]	0.50/–
III	0.06	130.62	0.904/0.818	0.71/0.70	1.0	1.400[b]/1.350[c]	0.44/–

[a] ($E^1_{1/2}$) is the first anodic half wave potential; (I_c/I_a) is the ratio of currents of the reverse cathode and direct anode peaks; (n) is the number of electrons of the first anode stage with respect to the standard ferrocene; (E^2_p) is the potential of the second oxidation peak. [b] Quasi-reversible process. [c] Irreversible peak.

478 , 448 w. ^{1}H NMR spectrum, δ, ppm: 1.42 s (18H, *t*-Bu), 2.37 s [9H, CH_3, Sb(*p*-Tol)$_3$], 6.59 s (2H, C_6H_2), 7.24 d [6H, Sb(*p*-Tol)$_3$, $^3J_{HH}$ 7.7 Hz], 7.66 d [6H, Sb(*p*-Tol)$_3$, $^3J_{HH}$ 7.7 Hz]. ^{13}C NMR spectrum, δ, ppm: 21.49 (CH_3, *p*-Tol), 29.57 (CH_3, *t*-Bu), 34.125 (C, *t*-Bu), 114.05 (CH, Ar), 129.77 [*m*-C, Sb(*p*-Tol)$_3$], 131.97 (C, Ar), 134.76 [*p*-C, Sb(*p*-Tol)$_3$], 134.97 [*o*-C, Sb(*p*-Tol)$_3$], 141.15 [*i*-C, Sb(*p*-Tol)$_3$], 145.42 (CO, Ar). Found, %: C 68.11; H 6.80; Sb 20.13. $C_{35}H_{41}O_2Sb$. Calculated, %: C 68.30; H 6.71; Sb 19.78.

(3,6-Cat)SbPh$_3$ (II) [3]. ^{1}H NMR spectrum, δ, ppm: 1.42 s (18H, *t*-Bu), 6.61 s (2H, C_6H_2), 7.36–7.60 m (9H, $H_{o,p}$, $SbPh_3$), 7.72-7.85 m (6H, $H_{m,}$ $SbPh_3$). ^{13}C NMR spectrum, δ, ppm: 29.57 (CH_3, *t*-Bu), 34.14 (C, *t*-Bu), 114.29 (CH, Ar), 129.10 ($C_{m,}$ Ph), 131.04 (C_p, $SbPh_3$), 132.12 (C, Ar), 135.01 (C_o, $SbPh_3$), 138.09 (C_i, $SbPh_3$), 145.27 (CO, Ar). Found, %: C 67.29; H 6.26; Sb 21.02. $C_{32}H_{35}O_2Sb$. Calculated, %: C 67.03; H 6.15; Sb 21.24.

(3,6-Cat)Sb(*p*-F-Ph)$_3$ (III). IR spectrum, ν, cm^{-1}: 1583 s, 1489 m, 1401 s, 1354 w, 1307 w, 1302 w, 1280 w, 1263 w, 1237 s, 1202 w, 1181 w, 1160 s, 1146 m, 1090 w, 1065 w, 1055 w, 1027 w, 1012 w, 977 s, 941 m, 925 w, 829 s, 811 m, 796 w, 695 s, 648 m, 609 w, 553 w, 511 s, 470 m, 450 w. ^{1}H NMR spectrum, δ, ppm: 1.41 s (18H, *t*-Bu), 6.63 s (2H, C_6H_2), 7.18 t [6H, $H_{m,}$ Sb(*p*-F-Ph)$_3$, $^3J_{HH}$ and $^3J_{HF}$ 8.6 Hz], 7.75 d.d [6H, H_o, Sb(*p*-F-Ph)$_3$, $^3J_{HH}$ 8.6, $^4J_{HF}$ 5.8 Hz]. ^{13}C NMR spectrum, δ, ppm: 29.56 (CH_3, *t*-Bu), 34.15 (C, *t*-Bu), 114.72 (CH, Ar), 116.66 [$C_{m,}$ Sb (*p*-F-Ph)$_3$, $^2J_{CF}$ 20.8 Hz,], 132.28 (C, Ar), 132.79 [C_i, Sb(*p*-F-Ph)$_3$, $^4J_{CF}$ 3.6 Hz], 136.93 [C_o, Sb(*p*-F-Ph)$_3$, $^3J_{CF}$ 8.0 Hz], 144.86 (CO, Ar), 164.75 [C_p, Sb(*p*-F-Ph)$_3$, $^1J_{CF}$ 252.6 Hz]. Found, %: C 61.07; H 5.01; Sb 19.52. $C_{32}H_{32}F_3O_2Sb$. Calculated, %: C 61.26; H 5.14; Sb 19.41.

NMR spectra were taken on a Bruker DPX-200 spectrometer with working frequencies 200 MHz (^{1}H) and 50 MHz (^{13}C) in $CDCl_3$ with TMS as an internal standard. IR spectra were recorded on a FSM-1201 Fourier spectrometer in mineral oil in KBr cells. Oxidation potentials were measured by the method of CVA in a three-electrode cell in argon atmosphere using a "IPC-pro" potentiostat and glass carbon (GC) working electrode of 2 mm diameter, platinum plate (S = 18 mm^2) auxiliary electrode, and (Ag/AgCl/KCl) with waterproof diaphragm as a reference electrode. Potential sweep rate 0.2 V s^{-1}. Background electrolyte 0.1 M Bu_4NClO_4 (99%, "Acros") was twice crystallized from aqueous EtOH and.dried in vacuum for 48 h at 50ºC. Dichloromethane and acetonitrile were purified by the known procedures [9]. Concentration of the antimony complexes was 0.003 mol l^{-1}.

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