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The binuclear trimethyl/triethylantimony(V) bis-catecholate derivatives of four-electron reduced 4,4'-di-(3-methyl-6-*tert*-butyl-*o*-benzoquinone)

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1. Introduction

The antimony complexes with different redox-active ligands derived from o-quinones and related ligands are the attractive prospective objects for the investigation of chemical, biochemical properties of antimony compounds and their application in medicine and pharmacy (including the investigations of antimicrobial, antiparasitic, antitumor and anticancer activities, biological toxicity, etc.) [1-6]. Complexes of triethylantimony(V) with 0,0redox-active ligands [7,8] are much less studied compared with triphenylantimony(V) compounds [9–16]. The tetradentate di-obenzoquinones are known as the interesting objects for the development of polynuclear molecules, molecular chains with different magnetic properties. The coordination chemistry of di-o-benzoquinones is much less investigated compared with their usual bidentate 0,0-analogues [17-21]. In previous papers, the binuclear antimony(V) bis-catecholates - derivatives of 4,4'-di-(3-methyl-6tert-butyl-o-benzoquinone), Q-Q (Scheme 1), and 4,4'-di-(3,6di-tert-butyl-o-benzoquinone)-ethylene were described [14,22].

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ABSTRACT

The reaction of 4,4'-di-(3-methyl-6-*tert*-butyl-o-benzoquinone) (Q-Q) with trimethyl- or triethylstibine proceeds as a two-electron oxidative addition of each quinone moiety and allows to prepare binuclear bis-catecholates R₃Sb(Cat-Cat)SbR₃ with a nearly quantitative yield (R = Me, **1**; R = Et, **2**). The products **1** and **2** were characterized by IR-, ¹H and ¹³C NMR spectroscopy. Molecular structure of triethylantimony (V) bis-catecholate **2** was confirmed by single-crystal X-ray analysis. Each Sb(V) atom adopts square pyramidal geometry with Cat moiety in basal positions, dihedral angle between Cat fragments is 74.27 (5)°. The oxidation of bis-catecholates by ferrocenium tetrafluoroborate or tetrabromo-*p*-benzoquinone leads to loss of one trialkylantimony(V) moiety forming paramagnetic salts containing one-side decoordinated mononuclear semiquinone-catecholato [R₃Sb(Cat-SQ)]⁻ anion detected by EPR. The oxidation of **1** by air oxygen allows to prepare mononuclear quinone-catecholate Me₃Sb(Cat-Q) (**3**). © 2010 Elsevier B.V. All rights reserved.

Several years ago we observed the reversible dioxygen binding by *o*-amidophenolates and some catecholates of triphenylantimony (V) [6]. The replacement of phenyls at central antimony atom with alkyl group affects the dioxygen reactivity of such complexes [7]. Triphenylantimony(V) bis-catecholate Ph₃Sb(Cat-Cat)SbPh₃ (derivative of Q-Q) was found to be air-stable both in solid and in solution. Meanwhile, it is well known that alkylantimony derivatives are less stable than phenyl ones. What will be properties of alkylantimonial complexes with Q-Q? Here we report on the synthesis and characterization of binuclear bis-catecholates of trimethyl- and triethylantimony(V) based on Q-Q ligand.

2. Results and discussion

A reaction of non-transition organometallics (e.g. dialkyl alkaliearth metals Me₂Zn, Me₂Cd, Et₂Zn, Et₂Cd, etc.) with *o*-benzoquinones was shown to proceed as 1,2- or 1,4-nucleophylic addition with formation of substituted 2-(alkylmetaloxy)-2-alkylcyclohexa-3,5-dienone or 2-(alkylmetaloxy)-4-alkylcyclohexa-2,5-dienone or as a single-electron oxidation of the organometallic compound with formation of organometallic derivatives of alkyl/aryloxyphenols [23,24]. However, it is not the case for a reaction of trialkylantimony compounds with *o*-quinones. The reaction of trialkylstibines is a two-electron oxidative addition (Scheme 1).

⁰⁰²²⁻³²⁸X/\$ - see front matter @ 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.jorganchem.2010.09.008

Table 1

The selected bond lengths and angles in 2



The dropwise addition of di-*o*-quinone Q-Q to toluene solutions of Me₃Sb or Et₃Sb is accompanied with a gradual colour change from green (quinone colour) to yellow or yellow-orange typical for non-transition metal complexes with catecholates.

After the change of toluene with hexane and storage of resulting solution at -20 °C, the yellow powders of **1** and **2** were obtained. An additional recrystallization of **2** from cyclohexane gave the yellow-orange needle crystals suitable for X-ray analysis. The characterization of products was made by IR, ¹H, ¹³C NMR spectroscopy (see Section 3). The reduction of both parts in dioquinone for complexes is evident from the absence of stretching vibrations of double C=O bonds of initial Q-Q (1648 and 1670 cm⁻¹) [25]. The ¹H NMR data shows the equivalence of two quinonato parts in complexes due to an mutual rotation of these CatSbR₃ fragments.

The molecular structure of complex $Et_3Sb(Cat-Cat)SbEt_3$ (2) is depicted in Fig. 1. The selected bond lengths are listed in Table 1. Each antimony atom is pentacoordinated and adopts a feebly distorted square pyramidal geometry. The base of pyramids is formed by atoms O(1), O(2), C(23), C(25) for Sb(1) and O(3), O(4), C(29), C (31) for Sb(2), the bond angles O(1)-Sb(1)-C(25), O(2)-Sb(1)-C(23), O(3)–Sb(2)–C(29) and O(4)–Sb(2)–O(31) lie in the range of 146.02(18)-151.8(2)°, the deviation of each antimony from the basal plane does not exceed 0.51–0.55(1) Å. The antimony–carbon bonds of apical ethyl groups (Sb(1)–C(27) and Sb(2)–C(33)) are shorter by 0.013–0.041 Å than the basal antimony–carbon bonds. The C–O bonds (1.354(4)-1.366(4) Å, being in average 1.359 Å) are long and typical for catecholate type of coordination of quinonato ligand [19] being considerably longer than in neutral Q-Q or in biso-simiquinonic dimethylthallium(III) complex Me₂Tl(SQ-SQ)TlMe₂ [26], and marginally shorter than in related triphenylantimony(V) bis-catecholate Ph₃Sb(Cat-Cat)SbPh₃ (1.351(1)-1.404(1) Å, av. 1.374 Å) [14]. The C–O bonds in neutral di-o-quinone O-Q are 1.211 (4)–1.220(4) Å [25] and the six-membered carbon rings show the quinoid bond alternation. This type of alternation is absent in Et₃Sb

Bond	Distance, [Å]	Angle	Value [°]
Sb(1)-O(1)	2.026(2)	O(1)-Sb(1)-O(2)	78.74(9)
Sb(1)-O(2)	2.031(2)	O(1)-Sb(1)-C(27)	101.85(15)
Sb(2)-O(3)	2.044(2)	O(2)-Sb(1)-C(27)	99.39(15)
Sb(2)-O(4)	2.035(2)	O(1)-Sb(1)-C(25)	149.06(17)
Sb(1)-C(23)	2.160(6)	O(2)-Sb(1)-C(25)	86.27(16)
Sb(1)-C(25)	2.124(5)	C(27)-Sb(1)-C(25)	107.2(2)
Sb(1)-C(27)	2.110(5)	O(1)-Sb(1)-C(23)	84.01(17)
Sb(2)-C(29)	2.139(4)	O(2)-Sb(1)-C(23)	151.8(2)
Sb(2)-C(31)	2.122(4)	C(27)-Sb(1)-C(23)	105.9(2)
Sb(2)-C(33)	2.105(5)	C(25)-Sb(1)-C(23)	97.7(2)
O(1) - C(1)	1.366(4)	O(4)-Sb(2)-O(3)	77.80(8)
O(3) - C(7)	1.354(4)	O(4)-Sb(2)-C(33)	100.99(16)
O(2) - C(2)	1.361(3)	O(3)-Sb(2)-C(33)	100.22(17)
O(4) - C(8)	1.356(3)	O(4)-Sb(2)-C(31)	149.56(14)
C(5) - C(11)	1.508(4)	O(3)-Sb(2)-C(31)	83.83(13)
C(1) - C(2)	1.379(5)	C(33)-Sb(2)-C(31)	106.1(2)
C(2) - C(3)	1.378(4)	O(4)-Sb(2)-C(29)	84.67(14)
C(3) - C(4)	1.394(4)	O(3)-Sb(2)-C(29)	146.02(18)
C(4) - C(5)	1.395(4)	C(33)-Sb(2)-C(29)	111.7(2)
C(5) - C(6)	1.393(4)	C(31)-Sb(2)-C(29)	97.9(2)
C(1) - C(6)	1.401(4)		
C(7) - C(8)	1.391(4)		
C(8)-C(9)	1.387(4)		
C(9) - C(10)	1.392(4)		
C(10)-C(11)	1.379(5)		
C(11)-C(12)	1.384(4)		
C(7)-C(12)	1.384(4)		

(Cat-Cat)SbEt₃, both six-membered carbon rings demonstrate aromatic character with av. C–C bond distance of 1.389 ± 0.011 Å. In Me₂Tl(SQ-SQ)TlMe₂ containing doubly-reduced form of Q-Q, the C–O bonds are of 1.267(4)–1.300(4) Å [26]. At the same time, mononuclear copper(II) complex of di-o-quinone, (bpy)Cu^{II}(Cat-Q), where bpy is 2,2'-bipyridine, display carbon-oxygen bonds in catecholate part to be 1.358(7) Å, and in quinone part -1.220(6) Å [27]. So, geometrical features of tetradentate ligand in antimony complex unequivocally confirm tetra-reduced bis-catecholate form of this ligand. Interesting observations concern the relative positions of halves in Cat-Cat ligand. The dihedral angle between Q moieties in neutral di-o-quinone Q-Q is very close to orthogonal (82.9°), the C-C distance between rings is 1.499(4) Å. Bis-o-semiquinonic Me₂Tl(SQ-SQ)TlMe₂ has a reduced dihedral angle 51.5° and the shortened C-C bond (1.465(6)Å) showing an enhanced conjugation between SQ halves. In the case of Et₃Sb(Cat-Cat)SbEt₃, the value of dihedral angle (74.3°) lie between that one for Q-Q and SO-SO while the length of C-C bond joining Cat moieties is 1.508(4)Å – the longest value among structurally characterized



Fig. 1. The drawing of molecular structure of 2. The atoms H are omitted for clarity.

derivatives of the di-o-quinone Q-Q. In both crystallographically independent molecules of triphenylantimony analogue Ph_3Sb (Cat-Cat)SbPh₃ the corresponding bonds are 1.501(1) and 1.461(1) Å (the dihedral angles are 82.6° and 79.9°, respectively) [14].

It is interesting that in crystal a solvated cyclohexane molecules are located between two molecules of **2** in such a manner that carbon atoms C(1s) are directed toward Sb(1) atoms (Fig. 2). The presence of this weak contact is clear from Fig. 2, however a distance C(1s)…Sb(1) is 4.42 Å that remarkably longer than the sum of Van-der-Vaals radii of carbon and antimony atoms (1.7 + 2.2 = 3.9 Å). The environment of other antimony atoms Sb(2) differs from that for atoms Sb(1). The basal planes formed by O(3), O(4), C(29), C(31) atoms in tetragonal pyramids of Sb(2) in neighboring molecules of **2** are coplanar and the coordination sphere of each Sb(2) atom in these molecules is completed by a weak intermolecular contacts Sb(2)…O(3) (4.29 Å). The distance between two Sb(2) atoms is 4.76 Å (also more than the 4.4 Å – a double Van-der-Vaals radius of Sb).

It is well known that o-quinones can be easily reduced to monoanionic o-semiquinone and dianionic catecholate forms. Paramagnetic o-semiquinones are gratifying objects for EPR spectroscopy. The neutral di-o-benzoquinone Q-Q was described to be a suitable starting compound for the preparation of mono-, di-, triand tetra- reduced derivatives by using potassium [25]. The EPR spectral investigations of monoreduced derivatives of [Q-SQ]⁻ type were described in ref. [28]. Authors have observed a hyper-fine coupling (h.f.c.) on one proton in 5th position of SQ ring, protons of two methyl groups in 3rd position of SO and 3'rd position of O mojeties [28]. The hyperfine structure in EPR spectra of such derivatives has a number of features including a less value of h.f.c. constant with one aromatic proton in SQ ring (2.6-2.9 G) compared with the value observed usually in EPR of o-semiguinones (>3 G); at the same time h.f.c. constants with methyl groups reach the quite big values up to 1.1-1.3 G. The tri-reduced potassium derivative [Cat-SQ]^{3–} reveals the rather different EPR spectral data ($A_{H(SQ)} = 3.37$ G, $A_{\text{Me(SO)}} = 0.33 \text{ G}, A_{\text{Me(Cat)}} = 0.19 \text{ G} \text{ and } A_{\text{H(Cat)}} = 0.23 \text{ G})$ [25].

Triethylantimony(V) complex Et₃Sb(Cat-Cat)SbEt₃ (**2**) can be easily oxidized to salts **2a** and **2b** containing catecholato-semiquinonato ion-radical using such oxidizers as ferrocenium tetrafluoroborate or tetrabromo-*p*-benzoquinone, respectively (Scheme 2). The EPR spectra of these salts have the same features as EPR of tripotassium salt $K_2^{\pm+}$ [Cat-SQ]^{3–}K⁺ (Table 2). X-band EPR spectrum of **2a** and its computer simulation are shown in Fig. 3. On the other hand, these spectral data are very close to those observed on salts with anion of [Ph₃Sb(Cat-SQ)^{2–} type [29] (Table 2). Worthy of note is that EPR spectra of **2a** and **2b** do not reveal any h.f.c. on magnetic nuclei of antimony atom (¹²¹Sb and ¹²³Sb). In the cases of paramagnetic complexes of Ph₃Sb(Cat-SQ)ML_n type containing chelating bonding between SQ part and metal fragment ML_n, EPR spectra contain a splitting on magnetic nuclei of metal M [29]. These facts allow to suppose a formation of ionic salts containing solvated anion [Et₃Sb(Cat-SQ)]⁻ and triethylantimony(V)-containing cation but not [Et₃Sb(Cat-SQ)SbEt₃]⁺ (Scheme 2). So, the oxidation of bis-catecholate **2** leads to the segregation of triethylantimony(V) dication forming [Et₃Sb-X]⁺ type cation.

The presence of h.f.c. with both methyl protons and proton in 5th position of second ring (Cat part of molecule) in all paramagnetic products point out the delocalization of odd electron over the whole molecule. The difference of EPR features of **2a**, **2b**, and related tripotassium salt K₂[Cat-SQ]K from that ones for complexes of monoreduced [Q-SQ]⁻ form suggests the different torsion angles between two parts of molecule in these derivatives because the possibility of delocalization of odd electron to the second ring (Q or Cat parts) depends on, in addition, the value of torsion angle between rings. The decrease of delocalization degree to the second ring in [Cat-SQ]³⁻ complexes in comparison with derivatives of [Q-SQ]⁻ allows to assume that torsion angles between Cat and SQ parts in **2a** and **2b** are more close to orthogonal than that for Q-SQ complexes.

The further heating of **2** with excess of oxidants leads to progressive disappearing sharp signal with concomitant growing wide signal with $g_{iso} = 2.0030$ and line width $\Delta H = 19$ G (Fig. 4) which can be attributed to a diradical bis-o-semiquinonato derivative [(SQ-SQ)]²⁻. However, the freezing of this solution leads to disappearance of EPR signal, probably due to antiferromagnetic coupling of paramagnetic centers to give a singlet diradical species most probably without helated tralkylantimony (in other words, outside the inner coordination sphere).

Trimethylantimony(V) bis-catecholate **1** reacts with above mentioned oxidants under stricter conditions (heating of toluene solution up to 70 °C) also with decomposition of catecholato-antimony moiety forming anions $[Me_3Sb(Cat-SQ)]^-$ **1a**, **1b**. However, they are not stable at those conditions and undergo decomposition to diamagnetic products.

In contrast to air-stable triphenylantimony bis-catecholate Ph₃Sb(Cat-Cat)SbPh₃ [14], **1** reacts slowly with dioxygen. But in this case, we have no found the formation of spiroendoperoxides as described in refs. [6,30]. The reaction of bis-catecholate **1** with air oxygen leads to loss of one trimethylantimony group forming cherry-red colored quinone-catecholate (Me₃Sb(Cat-Q))



Fig. 2. Fragment of crystal packing of $2 \cdot C_6 H_{12}$.





(3) (Scheme 3). The ¹H NMR spectrum of **1** exposed to air undergoes the changes: the signals from protons of **1** decrease with simultaneous appearance and increasing of signals from quinone-catecholate **3**. Methyl and tert-butyl protons of Q moiety give singlets at 1.81 and 1.23 ppm, isolated proton of six-membered carbon cycle of Q give rise to singlet at 6.78 ppm; the corresponding groups in Cat moiety of **3** give singlets at 2.10, 1.43 and 6.40 ppm, respectively. So, the ¹H NMR spectral features of Me₃Sb(Cat-Q) **3** are very close to those for triphenylantimony analogue Ph₃Sb(Cat-Q) [14].

Quinone-catecholate **3** was also synthesized by the another method: a reaction between di-*o*-quinone Q-Q and Me₃Sb in equimolar ratio in toluene as it was described for its triphenylantimony analogue [14]. This complex is more stable than bis-catecholates **1**,**2** and can be stored on air in solution during few days. So, we may conclude that the replacement of phenyl groups at antimony atoms in bis-catecholate Ph₃Sb(Cat-Cat)SbPh₃ with alkyls (in **1** and **2**) leads to destabilization of such complexes. They loose easily one of two coordinated trialkylantimony(V) moieties under the oxidation forming mononuclear semiquinone-catecholato species [R₃Sb(Cat-SQ)]⁻ (the oxidant is ferrocenium tetrafluoroborate or tetrabromo-

lable 2
EPR spectral data of paramagnetic Cat-SO complexes and O-SO derivatives

Complex	g _{iso}	$A_{\rm H(5th)}$, G	$A_{Me(3rd)}$, G	$A_{\mathrm{Me}(3'\mathrm{rd})}$, G	$A_{\mathrm{H}(6'\mathrm{th})}$, G
2a	2.0034	3.69	0.398	0.317	0.307
2b	2.0036	3.77	0.402	0.320	0.307
1a	2.0037	3.72	_	_	-
1b	2.0036	3.60	_	_	-
K ₂ ⁺⁺ [Cat-SQ] ^{3-•} K ⁺ [25]	2.0050	3.37	0.33	0.19	0.23
Ph₃Sb[Cat-SQ]	2.0046	3.6	~0.4	~0.4	-
[Cp ₂ Co] ⁺ [29]					
Ph₃Sb[Cat-SQ]Li [29]	2.0033	3.3	~0.4	~0.4	-
Ph ₃ Sb[Cat-SQ]SnPh ₃ [29]	2.0037	3.4	0.4	0.4	0.4
Ph ₃ Sb[Cat-SQ]Mn(CO) ₃	2.0033	3.3			
(Ph ₃ P) [29]					
Ph₃Sb[Cat-SQ]	2.0050	3.0	~0.4	~0.4	-
Cu(Ph ₃ P) ₂ [29]					
[Q-SQ] ^{-•} K ⁺ [25,28]	2.0049	2.60	1.30	1.10	0.20
[Q-SQ] Cp ₂ Co ⁺ [28]	2.0048	2.60	0.95	0.95	-

p-benzoquinone) or quinone-catecholate R₃Sb(Cat-Q) (the oxidant is dioxygen of air).

3. Experimental

All manipulations were carried out under an air-free atmosphere. The solvents were purified using standard technique [31]. Me₃Sb and Et₃Sb were synthesized as described in [32]. The ¹H, ¹³C, ¹³C DEPT NMR spectra were registered using Bruker AVANCE DPX-200 spectrometer (with a TMS as internal reference and CDCl₃ as solvent). IR spectra were monitored in the 400–4000 cm⁻¹ range by a FSM 1201 Fourier-IR spectrometer in Nujol mulls and reported in cm⁻¹. X-band EPR spectral investigations were performed on Bruker EMX spectrometer.

X-ray diffraction data for $2 \cdot C_6 H_{12}$ were collected using Oxford Diffraction (Gemini S) diffractometer with graphite monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) and with CCD detector Sapphire III in



Fig. 3. X-band EPR spectrum of 2a, exp – experimental (toluene, 295 K) and sim – simulated (WINEPR SimFonia 1.25).



Fig. 4. The changes in EPR spectrum of **2a** during prolonged heating at $60 \degree C$ with FcBF₄ (toluene, 296 K, sweep width 90 G).

the ω -scan mode (with max $2\theta = 61^{\circ}$ resolution). X-ray data were collected at temperature 298 K. The crystal structure was solved by direct methods (Shelx97) [33] and refined by full matrix method (WinGX and Shelx97) [34]. The reflection data were processed using the analytical absorption correction algorithm [35]. All non-hydrogen atoms were refined with anisotropic approximation. The all of H atoms refined in the "riding-model" ($U_{iso}(H) = 1.2 U_{eq}(\text{carbon}) \text{Å}^2$ for aromatic hydrogen and 1.5 $U_{eq}(\text{carbon}) \text{Å}^2$ for alkyl hydrogen) [33]. The minimal R_1 -factor obtained for $\mathbf{1} \cdot C_6H_{12}$ corresponds to 0.056. Table 3 summarizes the crystal data and some details of the data collection and refinement for $\mathbf{2} \cdot C_6H_{12}$. Selected bond distances and angles are given in Table 1.

3.1. Synthesis of complex 1

A toluene solution of di-*o*-quinone Q-Q (0.177 g, 0.5 mmol, 20 ml of solvent) was slowly added with extensive stirring to a solution of Me₃Sb in toluene (0.166 g, 1.0 mmol, \sim 10 ml of solvent) till the green colour of solution (colour of free di-*o*-quinone) turned pale yellow. Toluene was removed in vacuum and



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Scheme 3.
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Table 3

	-
Crysta	allographic data on $2 \cdot C_6 H_{12}$.

Empirical formula	C ₃₇ H ₆₂ O ₄ Sb ₂		
Formula weight	1262.04		
Temperature, K	298(2)		
Wavelength, Å	0.71073		
Crystal system	Monoclinic		
Space group	P 1 2 ₁ /n 1		
Unit cell dimensions	$a = 15.7351(6)$ Å $\alpha = 90.00^{\circ}$		
	$b = 15.7502(6) \text{ Å } \beta = 108.733(4)^{\circ}$		
	$c = 16.7297(5) \text{ Å } \gamma = 90.00^{\circ}$		
Volume, Å ³	3926.5(2)		
Z	4		
Density (calculated), Mg/m ³	1.378		
Absorption coefficient, mm ⁻¹	1.409		
F(000)	1672		
Crystal size, mm ³	$0.2\times0.1\times0.08$		
Theta range for data collection	3.35–30.51°		
Completeness to $\theta = 30.51$	98.3%		
Reflections collected	27,857		
Independent reflections	11790 [R(int) = 0.0493]		
Absorption correction	CrysAlis RED		
Max. and min. transmission	0.77809; 1		
Refinement method	Full-matrix least-squares on F ²		
Data/restraints/parameters	27857/0/389		
Final R indices $[I > 2$ sigma $(I)]$	$R_1 = 0.0561, wR_2 = 0.0996$		
R indices (all data)	$R_1 = 0.1594, wR_2 = 0.1229$		
Goodness-of-fit on F ²	0.931		

residue was dissolved in hot hexane. After solution cooling to room temperature the pale yellow powder of **1** precipitated and it was collected, washed with cold hexane and dried in vacuum. Yield is 0.327 g (95.0 %). IR (nujol, cm⁻¹): 1549m, 1480m, 1404s, 1365w, 1354m, 1344m, 1291w, 1265s, 1245s, 1182s, 1096m, 1064s, 1025m, 964s, 854m, 822s, 743s, 710s, 686s, 628w, 611w, 592w, 574w, 555w, 537m, 517m, 488m, 466w, 420w. ¹H NMR (200 MHz, CDCl₃, δ , ppm): 1.37 (s, 18 H, 2 SbMe₃), 1.38 (s, 18 H, 2tBu), 1.98 (s, 6 H, 2 Me), 6.48 (s, 2 H, 2 C₆H₁). ¹³C NMR (50 MHz, CDCl₃, δ , ppm): 12.48 (CH₃ of SbMe₃), 13.88 (CH₃), 29.71 (C(CH₃)₃), 34.30 (C(CH₃)₃), 116.88 (CH Ar), 118.09 (Ar), 130.15 (Ar), 131.60 (Ar), 143.49 (C–O of Ar), 145.37 (C–O of Ar). ¹³C{¹H} NMR (50 MHz, CDCl₃, δ , ppm): 12.48, 13.88, 29.71, 116.88. Anal. Calcd for C₂₈H₄₄O₄Sb₂ (%): C, 48.87; H, 6.44; Sb, 35.39. Found: C, 49.00; H, 6.57; Sb, 35.23.

3.2. Synthesis of complex 2

A toluene solution of di-o-quinone Q-Q (0.177 g, 0.5 mmol, 25 ml of solvent) was slowly added with stirring to a solution of Et₃Sb in toluene (0.209 g, 1.0 mmol, 20 ml of solvent) till the green colour of solution turned yellow. Toluene was removed in vacuum and residue was dissolved in petroleum ether. Reaction mixture was stored at -18 °C for a night to give vellow-orange powder of 2 which was filtered off, washed with cold solvent and dried in vacuum. Yield is 0.360 g (93.2 %). IR (nujol, cm⁻¹): 1555m, 1480m, 1410s, 1385m, 1367m, 1356m, 1345m, 1296 w, 1271m, 1240s, 1189m, 1095m, 1063s, 967s, 844m, 823s, 756w, 740m, 719s, 685s, 622w, 609w, 595w, 563m, 536m, 523m, 465w, 420w. ¹H NMR (200 MHz, CDCl₃, δ , ppm): 1.38 (s, 18 H, 2tBu), 1.42 (t, ${}^{3}J_{HH} = 7.7$ Hz, 18 H, 6 Et), 1.92 (q, ${}^{3}J_{HH} = 7.7$ Hz, 12 H, 6 Et), 1.99 (s, 6 H, 2 Me), 6.46 (s, 2 H, 2 C₆H₁). ${}^{13}C$ NMR (50 MHz, CDCl₃, δ , ppm): 9.24 (CH₂CH₃), 13.29 (CH₃), 19.98 (CH₂CH₃), 29.76 (C(CH₃)₃), 34.30 (C(CH₃)₃), 116.57 (CH Ar), 118.07 (Ar), 129.95 (Ar), 131.37 (Ar), 143.68 (C–O of Ar), 145.79 (C–O of Ar). ${}^{13}C{}^{1}H$ NMR (50 MHz, CDCl₃, δ , ppm): 9.24, 13.29, 19.98, 29.76, 116.57. Anal. Calcd for C₃₄H₅₆O₄Sb₂ (%): C, 52.87; H, 7.31; Sb, 31.53. Found: C, 53.10; H, 7.22; Sb, 31.28.

The crystals suitable for a single-crystal X-ray analysis were grown by the prolonged recrystallization from a cyclohexane solution as a cyclohexane solvate $2 C_6 H_{12}$.

3.3. Synthesis of complex 3

3.3.1. Oxidation of 1 by air dioxygen

A pale yellow solution of **1** in CDCl₃ in NMR tube was opened to air. A slow steam of air was bubbled through this solution several times during two days. The colour of solution turned cherry-red. NMR spectra were recorded for this solution. The slow evaporation of solvent allowed to obtain dark cherry-red powder of 3.

3.3.2. Reaction of Q-Q with Me₃Sb in equimolar ratio

The toluene solutions of di-o-quinone Q-Q (0.089 g, 0.25 mmol, 10 ml of toluene) and Me₃Sb (0.042 g, 0.25 mmol, \sim 5 ml of solvent) were mixed together. A solution color turned cherry-red and after that toluene was changed with *n*-hexane. A cooling of this solution resulted in precipitation of dark cherry-red powder of **3** in nearly quantitative yield. The NMR spectral characteristic is the same as those recorded for sample of **3** prepared by method described in Section 3.3.1. ¹H NMR (200 MHz, CDCl₃, *δ*, ppm): 1.23 (s, 9 H, tBu), 1.36 (s, 9 H, SbMe₃), 1.43 (s, 9 H, tBu), 1.81(s, 3 H, Me), 2.10 (s, 3 H, Me), 6.40 (s, 1 H, C₆H₁), 6.78 (s, 1 H, C₆H₁). ¹³C NMR (50 MHz, CDCl₃, δ, ppm): 12.50 (CH₃ of SbMe₃), 13.14 (CH₃), 13.94 (CH₃), 29.29 (C(CH₃)₃), 30.37 (C(CH₃)₃), 34.42 (C(CH₃)₃), 34.94 (C(CH₃)₃), 114.29 (CH Ar of Cat moiety), 116.48 (Ar), 127.08 (Ar), 131.39 (Ar), 133.33 (Ar), 140.26 (CH Ar of Q moiety), 146.02 (C-O Ar of Cat moiety), 146.23 (Ar), 146.35 (C-O Ar of Cat moiety), 150.65 (Ar), 180.74 (C=O of Q moiety), 182.03 (C=O of Q moiety). ¹³C{¹H} NMR (50 MHz, CDCl₃, δ, ppm): 12.50, 13.14, 13.94, 29.29, 30.37, 114.29, 140.26. Anal. Calcd for C₂₅H₃₅O₄Sb (%): C, 57.60; H, 6.77; Sb, 23.36. Found: C, 57.81; H, 6.90; Sb, 23.13.

4. Conclusions

The new binuclear bis-catecholate complexes of trimethyl- and triethylantimony(V) of R₃Sb(Cat-Cat)SbR₃ type were synthesized with a quantitative yield by oxidation reaction of corresponding trialkylstibines with di-o-quinone 4,4'-(3-methyl-6-tert-butyl-obenzoguinone). The reaction proceeds as a two-electron oxidative addition. The oxidation of complexes by tetrabromo-p-benzoquinone or ferrocenium cation leads to loss of one trialkylantimony moiety with formation of mononuclear semiquinonato-catecholato [R₃Sb(Cat-SQ)]⁻ species while air oxidation allows to obtain mononuclear quinone-catecholate Me₃Sb(Cat-Q).

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Appendix A. Supplementary data

The CCDC-781881 (2 C_6H_{12}) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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