

Triphenylantimony(V) 6-alkoxymethyl-3,5-di-*tert*-butylcatecholates. Structure and redox-properties

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ABSTRACT

A number of mononuclear triphenylantimony(V) 3,5-di-*tert*-butylcatecholates of the type (6-AlkOCH₂-3,5-DBCat)SbPh₃ functionalized with alkoxymethyl group in the 6th position of aromatic ring in catecholato ligand, where Alk = Me (**1**), Et (**2**), *i*Pr (**3**), *t*Bu (**4**), *n*-Hexyl (**5**), and binuclear bis-catecholate Ph₃Sb(3,5-DBCat-CH₂OCH₂-3,5-DBCat)SbPh₃ (**6**) have been synthesized and characterized in details. The molecular structures of **1**·0.5 (*n*-hexane), **2**, **3**, **4**, **5**·2MeOH, **6**·2 (*n*-hexane) and **6**·acetone have been determined by means of single-crystal X-ray analysis. The presence of alkoxymethyl-group in catecholate ligand does not lead to its coordination to the central antimony atom. Complexes **1**–**4** and **6** possess pentacoordinated environment of the central antimony atoms varying from the trigonal bipyramidal to the distorted tetragonal pyramidal. In crystal, molecules of complexes **1**–**5** form pairs where the “C_{Ph}–H ... π-system” interactions were found. The coordination environment of the central antimony atom in **5**·2MeOH is a distorted octahedral with coordinated methanol; the second methanol molecule is fixed between the hydroxyl group of coordinated methanol and the oxygen atom of hexyloxymethyl-group in the 6th position of catecholate ligand through the intramolecular hydrogen bonding.

The electrochemical oxidations of complexes **1**–**4** proceed as two one-electron oxidations (the quasi-reversible oxidation “catecholate/*o*-semiquinolate” and the irreversible oxidation “*o*-semiquinolate/*o*-benzoquinone”). The first half-wave potential ($E_{1/2}^1$) depends weakly on the alkoxy substituent in AlkO-CH₂ group due to a weak inductive effect of AlkO group to the catecholate aromatic ring through the methylene linker. For binuclear bis-catecholate **6**, the first redox stage is two-electronic quasi-reversible peak without the separation of two stages into two one-electron processes, which indicates the absence of the electronic interaction between the two catecholate fragments.

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1. Introduction

The investigation of transition metal and main group metal complexes with redox-active ligands of *o*-quinone type (*o*-quinones, *o*-iminoquinones, α -diimines) remains attractive for scientific groups around the world due to the variety of structural, electronic types displayed by these compounds and the tuning the properties by redox active ligands [1]. The redox-active *o*-quinone type ligands allow to extend the redox-properties of main group

metal compounds and lead to the appearance of chemical properties observed usually for transition metal compounds: for example, the cycloaddition of different alkynes [2]; the oxidative addition of alkyl halides [3], allyl halides [4] and isothiocyanates [5]; the reversible binding of nitrogen (II) oxide [6]; catalytic hydroamination and hydroarylation [7] etc. One more unusual chemical behaviour of main group metal complex with *o*-quinonato ligand is a reversible molecular oxygen binding by antimony(V) *o*-amido-phenolates and catecholates [8]. It was shown that the functionalization of redox active 3,6-di-*tert*-butylcatecholate ligand with different electron-acceptor or electron-donor groups in 4th and 5th positions of aromatic ring in antimony(V) catecholates allows to affect dramatically the redox-behaviour of such complexes as well

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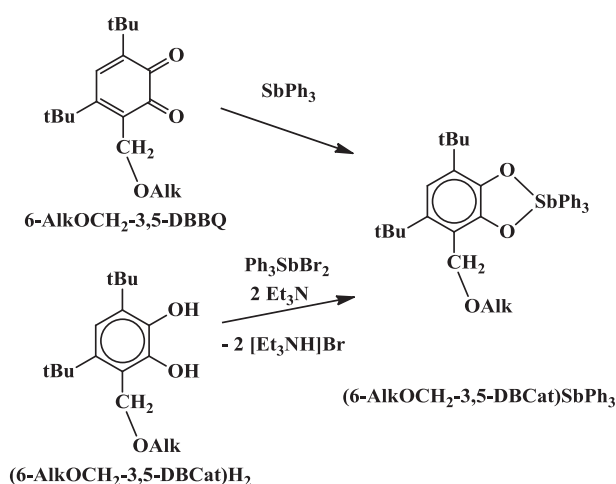
as their ability to bind molecular oxygen [9] and to be scavengers of radicals in different processes [10] including lipid peroxidation [11]. From the view point of molecular structure, triorganylantimony(V) catecholates demonstrate the great structural diversity: depending on the steric shielding of the central metal atom and the presence of different acceptor/donor substituents in catecholate ligand they are able to form either monomeric units with a considerable distortion of the metal coordination geometry or supramolecular assemblies in the crystal as a result of the molecular association [12]. Some mono- or binuclear antimony catecholate complexes have been shown to act as new molecules-sensors, for example, for fluoride ions [13].

One of the promising methods for the functionalization of catechols and their oxidized analogues *o*-benzoquinones is the insertion of different functional groups to the 6th position of aromatic ring by the alkylation reaction [14]. The application of 6-alkoxymethylated 3,5-di-*tert*-butylcatechols/*o*-benzoquinones in the antimony coordination chemistry should allow fine modification of the redox properties of the corresponding antimony(V) catecholates. In the present paper we report a series of new functionalized mononuclear triphenylantimony(V) 6-alkoxymethyl-3,5-di-*tert*-butylcatecholates of the type (6-AlkOCH₂-3,5-DBCat)SbPh₃ and their binuclear analogue Ph₃Sb(3,5-DBCat-CH₂OCH₂-3,5-DBCat)SbPh₃.

2. Results and discussion

2.1. Synthesis and characterization

In the present work a row of new 6-alkoxymethyl-3,5-di-*tert*-butylcatechols, (6-AlkOCH₂-3,5-DBCat)H₂, and 6-alkoxymethyl-3,5-di-*tert*-butyl-*o*-benzoquinones, 6-AlkOCH₂-3,5-DBBQ, containing the additional alkoxy-group at methyl in 6th position of redox-active ligand was synthesized in order to investigate the molecular structure and electrochemical properties of their triphenylantimony catecholato complexes. Triphenylantimony(V) catecholates can be synthesized starting from the corresponding substituted catechols and Ph₃SbHal₂ in the presence of a base or from *o*-benzoquinones and triphenylstibine [15]. Catecholates **1** [14b], **2–5** were prepared from the corresponding functionalized *o*-benzoquinones 6-AlkOCH₂-3,5-DBBQ and Ph₃Sb (Scheme 1) in toluene solution with good yields (more 80%). The exchange reaction between 6-alkoxymethyl-3,5-di-*tert*-butylcatechols, Ph₃SbBr₂ in the presence of two equivalents of triethylamine (Scheme 1) also leads



Scheme 1. The synthesis of triphenylantimony(V) catecholates.

to the formation of aimed triphenylantimony(V) 6-alkoxymethyl-3,5-di-*tert*-butylcatecholates (6-AlkOCH₂-3,5-DBCat)SbPh₃ displaying the same spectroscopic characteristics. Binuclear bis-catecholate **6** was synthesized from bis-*o*-benzoquinone 3,5-DBBQ-CH₂OCH₂-3,5-DBBQ and Ph₃Sb in the molar ratio of 1:2.

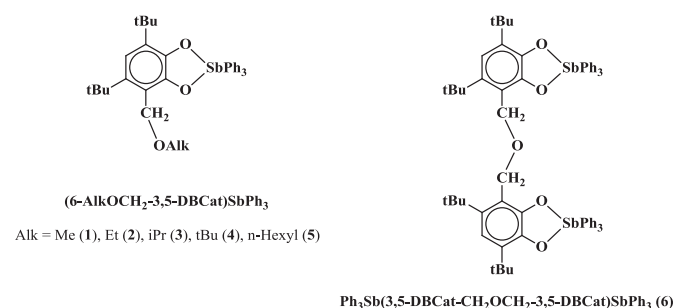
Mononuclear catecholato complexes **1–5** and binuclear bis-catecholate **6** (Scheme 2) were characterized by means of IR, ¹H and ¹³C NMR spectroscopy and elemental analysis.

The IR spectra of complexes contain set of bands of all structural fragments in complexes. The stretching vibrations of ordinary C–O bonds of catecholato ligands lie in the range of 1100–1250 cm⁻¹. At the same time, the vibrations of double bonds C=O of initial *o*-benzoquinones (1620–1670 cm⁻¹) are not observed in IR spectra of **1–6** that confirms the reduction of *o*-quinone ligands. The ¹H NMR spectra of complexes have distinctive resonances of all functional groups in complexes. The methylene group of Ar-CH₂-O fragment appears as singlet at 4.77–4.86 ppm in mononuclear complexes **1–5**, the single proton of aromatic cycle gives rise to singlet at 6.73–6.74 ppm. It should be noted that two *tert*-butyl groups protons appear as singlet at 1.43 ppm in ¹H NMR spectrum of methoxymethyl-functionalized complex **1**, as broadened singlet at 1.43 ppm in ethoxymethyl- and isopropoxymethyl-substituted complexes **2** and **3**, while these *tert*-butyl groups protons become distinguishable and appear as two singlets at 1.42 and 1.43 ppm in *tert*-butoxymethyl-substituted complex **4**. In binuclear complex **6** methylene protons singlet is up-shifted to 5.09 ppm, the singlet from aromatic protons of two C₆H₁ moieties is shifted to 6.64 ppm; *tert*-butyl group protons demonstrate two singlets at 1.30 and 1.46 ppm.

2.2. X-ray structures

The X-ray suitable crystals of complexes were grown from *n*-hexane for **2–4** and **6**. The molecular structure of complex **1** was reported previously [14b]. Crystals of complexes **1** and **6** contain 0.5 and 2 molecules of solvated *n*-hexane respectively per one complex molecule (1·0.5 (*n*-hexane), 6·2 (*n*-hexane)); crystals of **2–4** do not contain solvent. The recrystallization of binuclear complex **6** from acetone gave crystals 6·acetone with solvated acetone molecule. Hexoxymethyl-containing complex **5** does not crystallize in such solvents as *n*-hexane, toluene, chloroform, and it was crystallized from methanol as the solvate 5·2MeOH. The molecular structures of complexes **2–4** are shown on Fig. 1, the molecular structure of **6** in crystals 6·2 (*n*-hexane) – on Fig. 2, and the molecular structure of 5·2MeOH – on Fig. 3. The selected bond lengths for complexes are given in Table 1. The experimental and structure refinement details are summarized in Table S1 of ESI.

The X-ray quality crystals of methoxymethyl-containing catecholate **1** contain conformational isomers with different position of methoxymethyl-group toward the plane of catecholate ligand



Scheme 2. 6-Alkoxymethyl-substituted triphenylantimony(V) catecholato complexes.

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