

Oxidative addition reaction of *o*-quinones to triphenylantimony: novel triphenylantimony catecholate complexes

Vladimir K. Cherkasov, Ekaterina V. Grunova, Andrey I. Poddel'sky*, Georgy K. Fukin, Yury A. Kurskii, Ludmila G. Abakumova, Gleb A. Abakumov

G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Laboratory of the Chemistry of Organoelemental Compounds, 49 Tropinina Street, 603950 Nizhny Novgorod, Russia

Received 15 September 2004; accepted 22 November 2004

Available online 7 February 2005

Abstract

New catecholate Sb(V) complexes triphenyl(3,6-di-*tert*-butylcatecholato)antimony(V) $\text{Ph}_3\text{Sb}(3,6\text{-DBCat})$ (**1**) and triphenyl(perchloroxanthrenecatecholato)antimony(V) $\text{Ph}_3\text{Sb}(\text{O}^X\text{Cat}_{\text{Cl}})$ (**2**) were synthesized by the oxidative addition reaction of corresponding *o*-quinones (3,6-di-*tert*-butyl-*o*-benzoquinone and perchloroxanthrenequinone-2,3) with triphenylantimony. Catecholates **1** and **2** can alternatively be synthesized by reacting the appropriate thallium catecholate with triphenylantimony dichloride. The oxidative addition reaction of an equimolar ratio of 4,4'-di-(3-methyl-6-*tert*-butyl-*o*-benzoquinone) and triphenylantimony yielded 4-(2-methyl-5-*tert*-butyl-cyclohexadien-1,5-dion-3,4-yl)-(3-methyl-6-*tert*-butyl-catecholato)triphenylantimony(V) $\text{Ph}_3\text{Sb}(\text{Cat-Q})$ (**3**); in the case of a 1:2 molar ratio, complex 4,4'-di-[(3-methyl-6-*tert*-butyl-catecholato)triphenylantimony(V)] $\text{Ph}_3\text{Sb}(\text{Cat-Cat})\text{SbPh}_3$ (**4**) resulted. Complexes **1–4** were characterized by IR- and ^1H NMR spectroscopy. Molecular structures of **1**, **2** and **4** were determined by X-ray crystallography to be a distorted tetragonal-pyramidal.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Antimony; *o*-Quinones; Catecholates; Oxidative addition; X-ray diffraction

1. Introduction

The chemistry of Sb(V) catecholate complexes is very interesting but little has been published in this field of antimony chemistry. Related scientific literature has shown some methods for preparation of Sb(V) catecholates. The reaction of triphenylantimony dichloride and pyrocatechol in the presence of ammonia yielded the partially hydrated product – triphenylantimony catecholate hemihydrate $[\text{Ph}_3\text{Sb}(\textit{o}\text{-O}_2\text{C}_6\text{H}_4)]_2 \cdot \text{H}_2\text{O}$ [**1**]. As Holmes et al. [**2**] have reported, the reaction of Ph_3SbCl_2 with naphthalenediol in the presence of Et_3N leads to the isolation of the six-coordinated hypervalent anionic

stiborane $[\text{Ph}_3\text{Sb}(\text{Cl})(\textit{o}\text{-O}_2\text{C}_{10}\text{H}_6)][\text{Et}_3\text{NH}]$. The same authors synthesized $\text{Ph}_3\text{Sb}(\textit{o}\text{-O}_2\text{C}_6\text{H}_3\text{-4-NO}_2)$ by the same way from Ph_3SbCl_2 with 4-nitrocatechol in the presence of Et_3N [**3**]. The oxidation of elemental antimony by the *o*-quinones $\textit{o}\text{-O}_2\text{C}_6\text{Y}_4$ ($\text{Y} = \text{Cl}$ or Br) in diethyl ether yields the unusual antimony(V) products $\text{Sb}(\textit{o}\text{-O}_2\text{C}_6\text{Y}_4)_{2.5} \cdot n\text{Et}_2\text{O}$ ($\text{Y} = \text{Cl}$, $n = 1.5$, $\text{Y} = \text{Br}$, $n = 1$) [**4**]. Authors [**4**] also have synthesized antimony(III) derivatives $\text{Sb}(\text{Cat})\text{X}$ (Cat is the substituted catecholate dianion) by the reactions of the same quinones and 3,5-di-*tert*-butyl-*o*-benzoquinone with Sb(0) and 0.5X_2 ($\text{X} = \text{Br}$ or I). The six-coordinate antimony(V) catecholate complexes of $\text{R}_3\text{Sb}(\text{Cat})\text{L}$ species reported in [**5**] were synthesized by the oxidation of R_3Sb ($\text{R} = \text{Ph}$, Me) with *tert*-butylhydroperoxide in the presence of pyrocatechol and neutral donor ligands L (Py, DMSO

* Corresponding author. Tel.: +7(8312)127682; fax: +7(8312)127497.
E-mail address: aip@imoc.sinn.ru (A.I. Poddel'sky).

etc.). Holmes et al. [2] used the oxidative addition reaction of tetrachloro-*o*-benzoquinone with the corresponding stibole to form $\text{Ph}_3\text{Sb}(o\text{-O}_2\text{C}_6\text{Cl}_4)$ and $\text{PhSb}(o\text{-O}_2\text{C}_6\text{Cl}_4)(\text{C}_{12}\text{H}_8)\cdot 0.25\text{C}_6\text{H}_6\cdot 0.25\text{CH}_2\text{Cl}_2$. Later, Gibbons et al. [6] carried out the oxidative addition reaction between SbPhCl_2 and tetrachloro-*o*-benzoquinone in an ether solution, yielding six-coordinate tetrachlorocatechol species $\text{PhSb}(o\text{-O}_2\text{C}_6\text{Cl}_4)\text{Cl}_2\cdot\text{Et}_2\text{O}$. This paper focuses on synthesizing novel triphenylantimony complexes with some *o*-benzoquinones and determination of their molecular structures.

2. Results and discussion

2.1. Syntheses and characterizations

Catecholates complexes **1** and **2** can be prepared in different ways. The first way is the oxidative addition reaction of triphenylantimony with the corresponding *o*-quinones (3,6-di-*tert*-butyl-*o*-benzoquinone **1a** and perchloroxanthrenequinone-2,3 **2a**) at ambient temperature in a toluene solution (Scheme 1).

Alternatively, complexes **1** and **2** can be obtained from the appropriate thallium catecholates [7] and triphenylantimony dichloride by the exchange reaction. In both cases after a number of steps (see Section 3), the

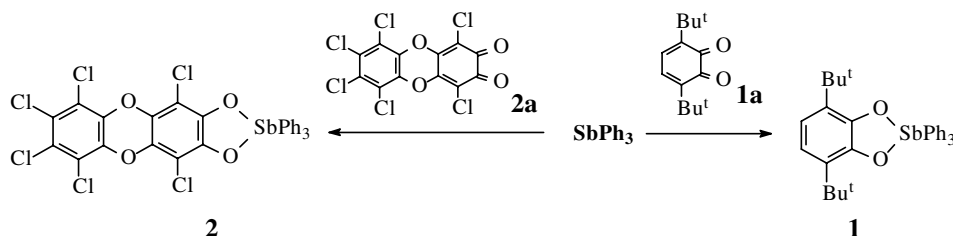
slow evaporation of the toluene solution of the complexes **1** and **2** afforded microcrystalline material that was identified by IR-, ^1H NMR spectroscopy and elemental analysis. Molecular structures of **1** and **2** were determined by X-ray crystallography.

In the case of di-*o*-quinone 4,4'-di-(3-methyl-6-*tert*-butyl-*o*-benzoquinone) (**3a**) the oxidative addition reaction to triphenylantimony may be performed with a different molar ratio of reagents. Interaction of **3a** and SbPh_3 in a 1:1 ratio yielded the quinono-catecholato complex **3**. On the other hand, the reaction of these reagents in a 1:2 molar ratio resulted in the di-catecholato complex **4** (Scheme 2).

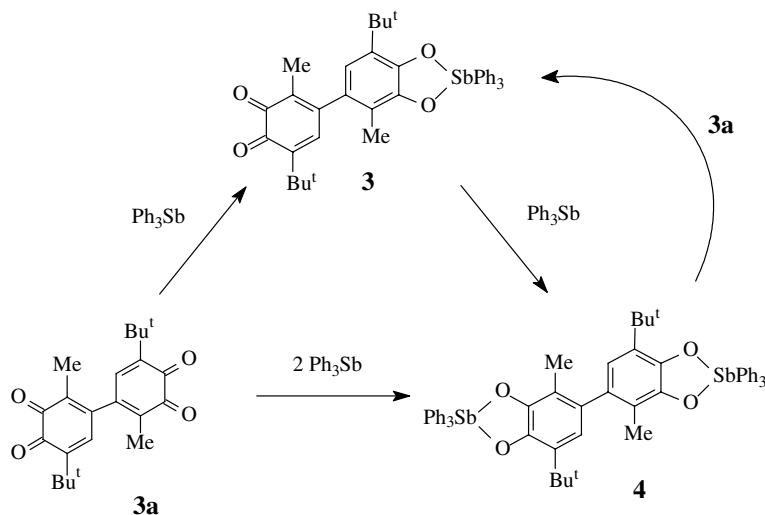
Compound **3** also can be obtained by the reaction of dicatecholates **4** with the initial di-*o*-quinone **3a**. The alternate way to synthesize **4** is the addition of triphenylantimony to the quinono-catecholato complex **3** (Scheme 2).

Complexes **3** and **4** have been isolated as air stable solids and identified by IR-, UV-visible and ^1H NMR spectroscopy and elemental analysis. The molecular structure of complex **4** was determined by X-ray structural analysis.

The formation of complex **3** is evident from a number of typical bands of its IR spectra in the range of 700–1600 cm^{-1} [8,9]. According to IR spectroscopic data the complex **3** has two kinds of absorption bands of



Scheme 1.



Scheme 2.

the carbon–oxygen vibrations ($\nu(\text{C}=\text{O})$ 1630, 1655, 1675, 1680 cm^{-1} and $\nu(\text{C}-\text{O})$ 1260, 1330 cm^{-1}).

The ^1H NMR spectrum of complex **4** in CDCl_3 shows the presence of two equal methyl and two equal *tert*-butyl groups of both catecholato fragments at 2.13 and 1.43 ppm, respectively. Carbon ring protons of both catecholato fragments have resonance at 6.54 ppm. The ^1H NMR spectrum of complex **3** in CDCl_3 confirms the presence of quinonato and catecholato fragment protons with equal intensity and different chemical shifts (δ) relative to SiMe_4 . The *tert*-butyl group protons of quinonato (Q) and catecholato (Cat) fragments have resonance at 1.22 and 1.43 ppm, respectively; for the analogous fragments (Q and Cat) the methyl group protons have chemical shifts at 1.82 and 2.23 ppm, respectively. Moreover, the ^1H NMR spectrum of complex **3** confirms the presence of two different carbon ring protons H(5) and H(5') with resonance at 6.46 and 6.79 ppm, respectively for catecholato and quinonato fragments (Fig. 1). ^1H NMR spectra of **3** and **4** contain phenyl group proton peaks at 7.46–7.84 and 7.43–7.86 ppm, respectively.

The electronic spectra of complexes **3** and **4** show a series of intense bands and shoulders (Fig. 2). Complex **3** exhibits three high intensity bands [λ/nm ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$), 288 (0.72×10^4), 400 (0.36×10^4) and 505 (0.305×10^4) in toluene at 290 K], complex **4** exhibits one very high intensity band [λ/nm ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$), 291 (2.21×10^4) in toluene at 290 K]. The electronic spectrum of the initial 4,4'-di-(3-methyl-6-*tert*-butyl-*o*-benzoquinone) **3a** is also shown in Fig. 2. Di-*o*-quinone

3a exhibits two high intensity bands [λ/nm ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) 288 (0.72×10^4) and 417 (0.36×10^4) in toluene at 290 K]. There are no absorptions above 650 nm for each of **3**, **4** and **3a**. It is worthy to note that UV–visible spectrum of **3** displays intense charge-transfer (CT) absorption with maximum at 505 nm ($\epsilon = 0.305 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), besides the typical bands of catecholato and quinone absorption.

2.2. Crystal structures

The crystal structures of **1**, **2** and **4** were determined by single-crystal X-ray diffraction analysis. Molecular structures of **1**, **2** and **4** are depicted in Figs. 3, 4 and 6,

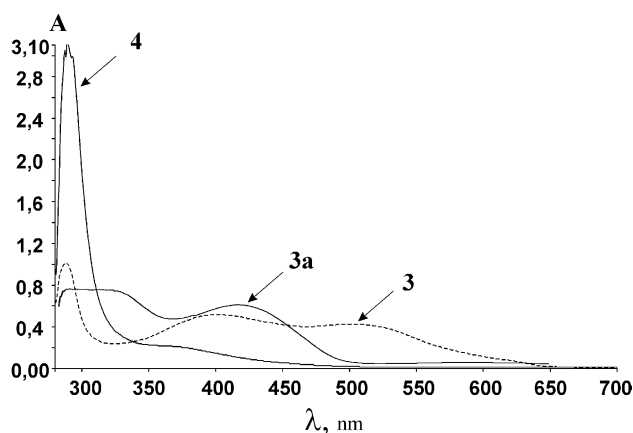


Fig. 2. Visible absorption spectra of **3**, **4** and **3a** in toluene at 290 K.

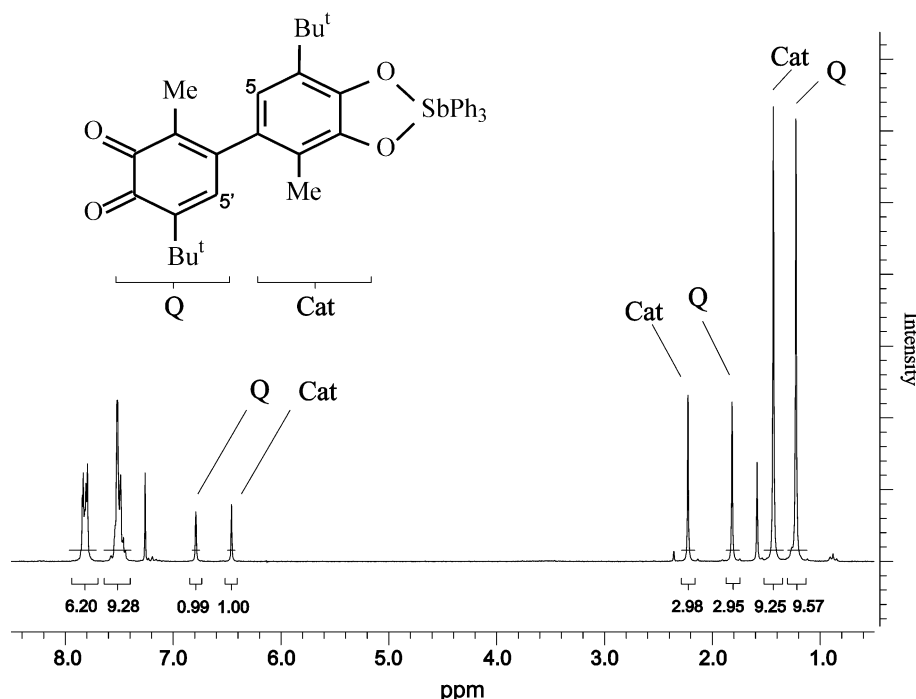


Fig. 1. ^1H NMR spectrum of **3** in CDCl_3 at ambient temperature. The labels under spectrum indicate the integral intensities of corresponding peaks.

respectively. Crystallographic data and structural determination details are given in Table 1. Tables 2–4 summarize the selected bond distances and angles in the molecules of **1**, **2** and **4**, respectively.

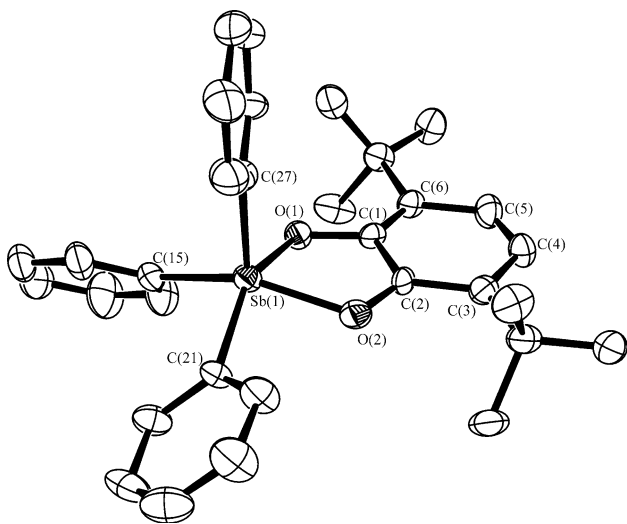


Fig. 3. An ORTEP view of **1** with 30% ellipsoid probability (H atoms are omitted).

According to X-ray diffraction analysis, complexes **1**, **2** and **4** form distorted tetragonal-pyramidal structures around the Sb atom. The catecholato oxygens and two phenyl groups for each molecule are arranged at the base of the pyramid. The third phenyl group occupies the axial position. The deviations of Sb atoms in **1**, **2** and **4** from basal planes are 0.496, 0.5 and 0.485–0.504 Å towards the axial phenyl groups for each molecule, respectively. The angles between the equatorial and axial substituents vary in the range of 98.7(1)–106.54(8)° for **1**, 91.82(7)–110.20(7)° for **2** and 92.1(3)–111.5(3)° for **4**. The geometries of the five-membered chelate metalocycles SbOOC in molecules **1**, **2** and **4** are not planar. The bend angles along the O...O line are 11.7° and 13.1° for the first and second independent molecules of **1**, respectively; 7.6° for **2**; vary from 9.0° to 17.9° for the first and second independent molecules of **4**. The similar bend angles in other catecholato fragments of Sb(V) compounds [5] vary in the range of 2.8–13.1°.

Crystals of **1** and **2** contain one solvent molecule of *n*-hexane and toluene, respectively, per two independent complex molecules.

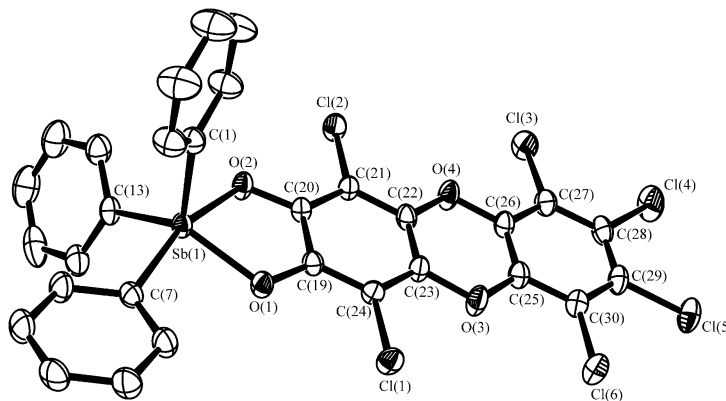


Fig. 4. An ORTEP view of **2** with 30% ellipsoid probability (H atoms are omitted).

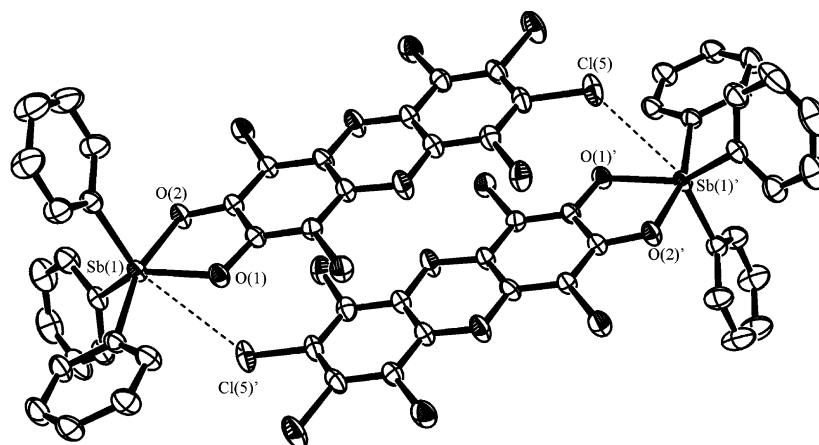


Fig. 5. The intermolecular interactions in crystals of **2** (H atoms are omitted).

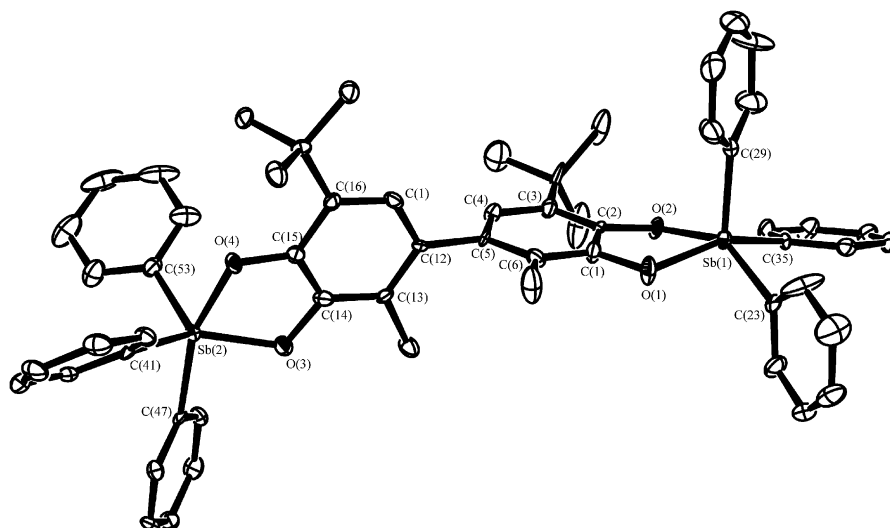
Fig. 6. An ORTEP view of **4** with 30% ellipsoid probability (H atoms are omitted).

Table 1

Summary of crystal and refinement data for complexes

	$\text{Ph}_3\text{Sb}(3,6\text{-DBCat}) \cdot 0.5\text{C}_6\text{H}_{14}$ ($1 \cdot 0.5\text{C}_6\text{H}_{14}$)	$\text{Ph}_3\text{Sb}(\text{OXCat}_{\text{Cl}}) \cdot 0.5\text{C}_7\text{H}_8$ ($2 \cdot 0.5\text{C}_7\text{H}_8$)	$\text{Ph}_3\text{Sb}(\text{Cat-Cat})\text{SbPh}_3$ (4)
Empirical formula	$\text{C}_{35}\text{H}_{42}\text{O}_2\text{Sb}$	$\text{C}_{33.5}\text{H}_{19}\text{O}_4\text{Cl}_6\text{Sb}$	$\text{C}_{58}\text{H}_{56}\text{O}_4\text{Sb}_2$
Formula weight	616.47	819.94	1060.53
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P1$	$P\bar{1}$	$P2_1/n$
<i>Unit cell dimensions</i>			
$a/\text{Å}$	10.2533(6)/110.4980(10)	9.1764(5)/116.6220(10)	16.057(2)/90
$b/\text{Å}$	12.5062(7)/107.9090(10)	13.8038(7)/100.5990(10)	18.431(3)/96.372(3)
$c/\text{Å}$	14.3225(8)/95.9690(10)	14.9300(7)/91.6920(10)	35.800(6)/90
Volume (Å ³)	1590.10(16)	1648.29(14)	10530(3)
Z	2	2	8
Density (calc.) (Mg/m ³)	1.287	1.652	1.338
Absorption coefficient (mm ⁻¹)	0.895	1.361	1.069
Crystal size (mm ³)	0.60 × 0.40 × 0.40	0.22 × 0.20 × 0.06	0.10 × 0.10 × 0.02
Reflections collected	16,850	17,443	48,458
Independent reflections	14,925 [$R_{\text{int}} = 0.0147$]	8573 [$R_{\text{int}} = 0.0225$]	15,201 [$R_{\text{int}} = 0.0958$]
Absorption correction	SADABS	SADABS	SADABS
Max. and min. transmission	0.7161 and 0.6158	0.9228 and 0.7539	0.9789 and 0.9006
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	14,925/67/692	8573/20/466	15,201/54/1153
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0243$, $wR_2 = 0.0628$	$R_1 = 0.0374$, $wR_2 = 0.0850$	$R_1 = 0.0712$, $wR_2 = 0.1312$
R indices (all data)	$R_1 = 0.0272$, $wR_2 = 0.0651$	$R_1 = 0.0495$, $wR_2 = 0.0900$	$R_1 = 0.1250$, $wR_2 = 0.1473$
Goodness-of-fit on F^2	1.041	1.024	1.106
Largest diff. peak and hole (e Å ⁻³)	0.623 and -0.325	0.847 and -0.323	1.364 and -1.110

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b \omega R = R(\omega F^2) = \{ \sum [\omega(F_o^2 - F_c^2)^2] / \sum [\omega(F_o^2)] \}^{1/2}; \omega = 1/[\sigma^2(F_o^2) + (aP)^2 + bP], P = [2F_c^2 + F_o^2]/3$$

$$^c S = \text{Goof} = \{ \sum [\omega(F_o^2 - F_c^2)^2] / (n - p) \}^{1/2}, \text{ where } n \text{ is the number of reflections, and } p \text{ is the number of refined parameters.}$$

2.2.1. The crystal structure of $\text{Ph}_3\text{Sb}(3,6\text{-DBCat})$ (**1**)

According to X-ray diffraction analysis there are two independent molecules of **1** which have slightly different geometrical parameters. The molecules in the crystal of complex **1** are isolated. The dihedral angle between the $\text{Sb}(1)\text{O}(1)\text{O}(2)$ and $\text{Sb}(1)\text{C}(15)\text{C}(21)$ planes in the first independent molecule is $140.5(1)^\circ$ while the same planes in the second independent molecule form a $140.9(1)^\circ$.

The catechol fragment in the first independent molecule has a very unusual geometry. The $\text{O}(1)\text{--C}(1)$ and $\text{O}(2)\text{--C}(2)$ distances are 1.364(3) and 1.319(3) Å; one of them is close to analogous distances in semiquinones (1.28–1.31 Å [10]), but the other is close to analogous distances in catecholates (1.33–1.39 Å [4,5,10]). The C–C distances in the six carbon ring C(1–6) have the bond lengths alternation. The C(1)–C(6) and C(4)–C(5) distances are

Table 2
Selected bond lengths (Å) and angles (°)

First independent molecule of 1			
Sb(1)–O(2)	2.010(2)	O(2)–Sb(1)–O(1)	78.99(8)
Sb(1)–O(1)	2.018(2)	O(2)–Sb(1)–C(27)	102.51(7)
Sb(1)–C(27)	2.118(1)	O(1)–Sb(1)–C(27)	98.70(7)
Sb(1)–C(21)	2.121(3)	O(2)–Sb(1)–C(21)	84.68(9)
Sb(1)–C(15)	2.149(2)	O(1)–Sb(1)–C(21)	152.37(7)
O(1)–C(1)	1.364(3)	C(27)–Sb(1)–C(21)	106.54(8)
O(2)–C(2)	1.319(3)	O(2)–Sb(1)–C(15)	148.73(6)
C(1)–C(6)	1.301(4)	O(1)–Sb(1)–C(15)	84.76(7)
C(1)–C(2)	1.448(4)	C(27)–Sb(1)–C(15)	106.26(6)
C(2)–C(3)	1.439(4)	C(21)–Sb(1)–C(15)	98.48(9)
C(3)–C(4)	1.426(5)		
C(4)–C(5)	1.327(5)		
C(5)–C(6)	1.459(4)		
Second independent molecule of 1			
Sb(2)–O(4)	2.029(2)	O(4)–Sb(2)–O(3)	78.82(8)
Sb(2)–O(3)	2.032(2)	O(4)–Sb(2)–C(59)	100.82(9)
Sb(2)–C(59)	2.100(2)	O(3)–Sb(2)–C(59)	101.88(8)
Sb(2)–C(53)	2.116(2)	O(4)–Sb(2)–C(53)	85.62(8)
Sb(2)–C(47)	2.157(2)	OC(59)–Sb(2)–C(53)	104.81(8)
O(3)–C(33)	1.412(4)	O(4)–Sb(2)–C(47)	150.35(7)
O(4)–C(34)	1.369(3)	O(3)–Sb(2)–C(47)	84.72(8)
C(33)–C(38)	1.342(4)	C(59)–Sb(2)–C(47)	106.64(9)
C(33)–C(34)	1.369(4)	C(53)–Sb(2)–C(47)	97.80(8)
C(34)–C(35)	1.481(4)	C(33)–O(3)–Sb(2)	114.78(18)
C(35)–C(36)	1.337(4)	C(34)–O(4)–Sb(2)	112.43(18)
C(35)–C(39)	1.468(5)		
C(36)–C(37)	1.452(5)		
C(37)–C(38)	1.343(5)		

Table 3
Selected bond lengths (Å) and angles (°) for **2**

Sb(1)–O(1)	2.022(2)	C(27)–C(28)	1.397(3)
Sb(1)–O(2)	2.088(1)	C(28)–C(29)	1.376(3)
Sb(1)–C(1)	2.099(2)	C(29)–C(30)	1.390(3)
Sb(1)–C(13)	2.111(2)	Cl(1)–C(24)	1.724(2)
Sb(1)–C(7)	2.130(2)	Cl(2)–C(21)	1.722(2)
O(1)–C(19)	1.347(2)	Cl(3)–C(27)	1.712(2)
O(2)–C(20)	1.336(2)	Cl(4)–C(28)	1.716(2)
O(3)–C(25)	1.370(3)	Cl(5)–C(29)	1.725(2)
O(3)–C(23)	1.389(3)	Cl(6)–C(30)	1.715(2)
O(4)–C(26)	1.370(3)		
O(4)–C(22)	1.385(3)	O(1)–Sb(1)–O(2)	78.44(5)
C(19)–C(24)	1.378(3)	O(1)–Sb(1)–C(1)	110.20(7)
C(19)–C(20)	1.409(3)	O(2)–Sb(1)–C(1)	91.82(7)
C(20)–C(21)	1.383(3)	O(1)–Sb(1)–C(13)	135.02(8)
C(21)–C(22)	1.388(3)	O(2)–Sb(1)–C(13)	84.44(7)
C(22)–C(23)	1.376(3)	C(1)–Sb(1)–C(13)	111.63(9)
C(23)–C(24)	1.387(3)	O(1)–Sb(1)–C(7)	87.18(7)
C(25)–C(30)	1.384(3)	O(2)–Sb(1)–C(7)	63.25(8)
C(25)–C(26)	1.386(3)	C(1)–Sb(1)–C(7)	101.26(8)
C(26)–C(27)	1.377(3)	C(13)–Sb(1)–C(7)	100.13(8)

1.301(4) and 1.327(5) Å, respectively. These length values are very close to the C=C distances in benzoquinones [11] and much less than the other C–C bonds (1.426(5)–1.459(4) Å) in this fragment. Apparently such extraordinary geometry of the first independent molecule of **1** is conditioned by crystal-packing effects, and this fragment is a catecholato ligand. IR-, ¹H NMR and EPR-spectroscopy data, also confirm the claimed catecholato structure.

Table 4
Selected bond lengths (Å) and angles (°)

First independent molecule of 4			
Sb(1)–O(2)	2.029(6)	C(14)–C(15)	1.392(1)
Sb(1)–O(1)	2.049(6)	C(15)–C(16)	1.415(1)
Sb(1)–C(29)	2.116(1)	C(16)–C(17)	1.366(1)
Sb(1)–C(23)	2.134(1)		
Sb(1)–C(35)	2.140(9)	O(2)–Sb(1)–O(1)	79.0(3)
O(1)–C(1)	1.375(1)	O(2)–Sb(1)–C(29)	99.7(3)
C(1)–C(2)	1.386(1)	O(1)–Sb(1)–C(29)	99.3(4)
C(1)–C(6)	1.397(1)	O(2)–Sb(1)–C(23)	147.0(3)
Sb(2)–O(3)	2.011(6)	O(1)–Sb(1)–C(23)	82.1(3)
Sb(2)–O(4)	2.056(6)	C(29)–Sb(1)–C(23)	109.9(4)
Sb(2)–C(53)	2.118(1)	O(2)–Sb(1)–C(35)	87.6(3)
Sb(2)–C(41)	2.144(1)	O(1)–Sb(1)–C(35)	154.2(3)
Sb(2)–C(47)	2.166(9)	C(29)–Sb(1)–C(35)	104.6(4)
O(2)–C(2)	1.366(1)	C(23)–Sb(1)–C(35)	98.4(4)
C(2)–C(3)	1.397(1)	O(3)–Sb(2)–O(4)	79.6(2)
O(3)–C(14)	1.404(1)	O(3)–Sb(2)–C(53)	111.5(3)
C(3)–C(4)	1.402(1)	O(4)–Sb(2)–C(53)	92.1(3)
C(4)–C(5)	1.383(1)	O(3)–Sb(2)–C(41)	137.4(3)
O(4)–C(15)	1.351(1)	O(4)–Sb(2)–C(41)	86.6(3)
C(5)–C(6)	1.388(1)	C(53)–Sb(2)–C(41)	109.1(4)
C(5)–C(12)	1.502(1)	O(3)–Sb(2)–C(47)	84.1(3)
C(12)–C(13)	1.378(1)	O(4)–Sb(2)–C(47)	161.5(3)
C(12)–C(17)	1.415(1)	C(53)–Sb(2)–C(47)	101.9(4)
C(13)–C(14)	1.388(1)	C(41)–Sb(2)–C(47)	99.7(4)
Second independent molecule of 4			
Sb(3)–O(5)	2.005(6)	C(66)–C(68)	1.534(1)
Sb(3)–O(6)	2.028(6)	C(66)–C(67)	1.552(1)
Sb(3)–C(93)	2.113(9)		
Sb(3)–C(81)	2.130(1)	O(5)–Sb(3)–O(6)	78.7(3)
Sb(3)–C(87)	2.154(1)	O(5)–Sb(3)–C(93)	110.9(3)
Sb(4)–O(7)	2.026(7)	O(6)–Sb(3)–C(93)	92.6(3)
Sb(4)–O(8)	2.030(6)	O(5)–Sb(3)–C(81)	136.8(3)
Sb(4)–C(99)	2.114(1)	O(6)–Sb(3)–C(81)	86.2(3)
Sb(4)–C(105)	2.130(1)	C(93)–Sb(3)–C(81)	110.0(4)
Sb(4)–C(111)	2.150(1)	O(5)–Sb(3)–C(87)	84.4(3)
O(5)–C(60)	1.368(1)	O(6)–Sb(3)–C(87)	161.7(3)
O(6)–C(59)	1.368(1)	C(93)–Sb(3)–C(87)	100.2(4)
O(7)–C(72)	1.392(1)	C(81)–Sb(3)–C(87)	101.5(4)
O(8)–C(73)	1.371(1)	O(7)–Sb(4)–O(8)	78.7(3)
C(59)–C(60)	1.405(1)	O(7)–Sb(4)–C(99)	99.0(4)
C(59)–C(64)	1.413(1)	O(8)–Sb(4)–C(99)	100.0(3)
C(60)–C(61)	1.380(1)	O(7)–Sb(4)–C(105)	81.9(3)
C(61)–C(62)	1.414(1)	O(8)–Sb(4)–C(105)	145.9(3)
C(61)–C(65)	1.483(1)	C(99)–Sb(4)–C(105)	110.7(4)
C(62)–C(63)	1.402(1)	O(7)–Sb(4)–C(111)	153.8(4)
C(62)–C(70)	1.461(1)	O(8)–Sb(4)–C(111)	86.0(3)
C(63)–C(64)	1.399(1)	C(99)–Sb(4)–C(111)	104.6(4)
C(64)–C(66)	1.515(1)	C(105)–Sb(4)–C(111)	100.0(4)

The second independent molecule also has different C–C distances in its 3,6-*tert*-butyl-catecholato fragment. The C(35)–C(36), C(37)–C(38) and C(38)–C(33) distances are 1.337(4), 1.343(5) and 1.342(4) Å and are smaller than the other bond lengths in this fragment (1.369(3)–1.481(4) Å). The O–C distances are 1.369(3) and 1.412(4) Å; similar to the same bond lengths in catecholato fragments (1.33–1.39 Å [4,5,10]). Apparently the second independent molecule of **1** has more delocalized electrons in the five-membered metallocycle Sb(2)O(3)O(4)C(33)C(34). The Sb–O distances in the

first independent molecule are 2.010(2) and 2.018(2) Å; somewhat shorter than the analogous distances in the second independent molecule of (2.029(2), 2.032(2) Å).

2.2.2. The crystal structure of $Ph_3Sb(O^XCat_{Cl})$ (**2**)

The dihedral angle between Sb(1)O(1)O(2) and Sb(1)C(7)C(13) planes is equal 134.2(1)°. The geometry of six-membered ring system C(22)C(23)O(3)C(25)–C(26)O(4) is close to planar; the bend angle along the O(3)...O(4) line is 0.5°.

The O(1)–C(19) and O(2)–C(20) distances are 1.347(2) and 1.336(2) Å, respectively. The C–C bond lengths in the C(19–24) carbon ring system vary in the range of 1.376(3)–1.409(3) Å, according to the lengths of aromatic C–C bonds. Thus, quinonato ligand has the catecholato form in complex **2**. The O(3)–C(23,25) and O(4)–C(22,26) distances vary in the range of 1.370(3)–1.389(3) Å and are similar to ordinary bonds [4,5,10]. The C(25–30) carbon ring system is also the aromatic system (1.38–1.40 Å). The Sb(1)–O(1,2) bond lengths are 2.022(2) and 2.088(1) Å, and are somewhat unequal as in complex **1**. The Sb–O bonds in the related complex $PhCl_2Sb(O_2C_6Cl_4)$ also are unequal (2.027(1), 1.991(1) Å [6]). It was found that there are the weak intermolecular interactions between neighbouring molecules in the crystal of complex **2**. The intermolecular Sb(1)...Cl(5)' [Sb(1)'...Cl(5)] distance is 3.966(1) Å, almost equal to the sum of van der Waals radii of Sb and Cl atoms (4.0 Å [12]) (Fig. 5).

2.2.3. The crystal structure of $Ph_3Sb(Cat-Cat)SbPh_3$ (**4**)

According to the X-ray diffraction analysis, complex **4** has two independent molecules whose geometrical parameters differ slightly. The dihedral angles between OSbO and $C_{basal}SbC_{basal}$ planes are equal 132.9°, 135.5°, 135.6° and 139.4° for both independent molecules. Thus the geometry of the coordinational environment in **4** is very similar to **1** and **2**. The apical Ph groups of each Sb(V) catecholato fragments occupy *trans* positions relatively to each other.

The O–C and C–C distances in the five-membered metallocycles are 1.351(1)–1.404(1) and 1.386(1)–1.405(1) Å, respectively, and are typical for catecholate complexes. The C(5)–C(12) and C(62)–C(70) bond distances between catecholate fragments are equal 1.502(1) and 1.461(1) Å, respectively. The dihedral angles between C(1–6) and C(12–17), C(59–64) and C(70–75) are equal 82.6° and 79.9°.

3. Experimental

3.1. General considerations

Triphenylantimony was prepared as described in [13]. 3,6-Di-*tert*-butyl-*o*-benzoquinone, perchloroxanthren-

equinone-2,3 and 4,4'-di-(3-methyl-6-*tert*-butyl-*o*-benzoquinone) were prepared according to literature procedures [14–16], respectively. Solvents were purified by standard methods [17]. Syntheses of complexes **1–4** were carried out in vacuum.

¹H NMR spectra were recorded on Bruker AVANCE DPX-200 spectrometer, using the CDCl₃ solvent and the internal standard tetramethylsilane. IR spectra were recorded on Specord M-80. Electronic absorption spectra of the complexes were recorded on a Perkin–Elmer Lambda 25 UV/Vis spectrometer (range: 220–1100 nm) at an ambient temperature. X-ray structure analysis was carried out on “Smart Apex” diffractometer (Bruker AXS).

3.2. Preparation of complexes

3.2.1. Triphenyl(3,6-di-*tert*-butylcatecholato)antimony(V) $Ph_3Sb(3,6-DBCat)$ (**1**)

Method 1. Oxidative addition reaction. Triphenylantimony (0.35 g, 1 mmol) was dissolved in dry toluene (20 ml). 3,6-Di-*tert*-butyl-*o*-benzoquinone (0.22 g, 1 mmol) dissolved in 20 ml of toluene was added dropwise to the triphenylantimony solution over a period of 10 min. The green color of free *o*-quinone lightened as each drop came into contact and react with the triphenylantimony solution. After the addition was complete, the reaction mixture became yellow. Removal of solvent under vacuum yielded a solid material. Recrystallization of this crude material yielded microcrystalline product. Yield 0.55 g (96%). Anal. Calc. for C₃₂H₃₅O₂Sb %: C, 66.80; H, 6.48; Sb, 21.12. Found: C, 66.46; H, 6.81; Sb, 21.44. IR (nujol, cm⁻¹): ν(C–O) 1245, 1265, 1315; ν(Sb–O) 650; ν(Sb–Ph) 445. ¹H NMR (CDCl₃), δ, ppm: 1.42 (s, 18 H, Bu^t); 6.61 (s, 2H, C₆H₂); 7.26–7.81 (m, 15H, aromatic). The recrystallization from hexane yielded yellow crystals suitable for X-ray analysis; m.p. 141–142 °C.

Method 2. Triphenylantimony dichloride (0.42 g, 1 mmol) was dissolved in dry THF (20 ml). 3,6-di-*tert*-butyl-*o*-benzoquinone (0.22 g, 1 mmol) was dissolved in 40 ml of dry THF and was placed into a tube with the excess of thallium amalgam. The mixture of quinone and thallium amalgam was shaken until the formation of appropriate yellow colored thallium catecholate [7]. Then the THF solvent of thallium catecholate was added to the antimony solution and mixture turned dark yellow. The solvent was replaced by toluene and the thallium chloride precipitated was filtered off under vacuum. After 3 hours the yellow crystals precipitated were filtered off, washed with cold toluene and dried under vacuum. The yield was 0.53 g, 92%.

3.2.2. Triphenyl(perchloroxanthrenecatecholato)antimony(V) $Ph_3Sb(O^XCat_{Cl})$ (**2**)

Method 1. Oxidative addition reaction. The synthesis and the product isolation of **2** were carried out similarly

to the synthesis 3.2.1, method 1 for **1**. Thus, the reaction of triphenylantimony (0.27 g, 0.75 mmol) and perchloroxanthrenequinone-2,3 (0.32 g, 0.75 mmol) yielded 0.56 g (97%) of yellow crystals; m.p. 203 °C. Anal. Calc. for $C_{33.5}H_{19}Cl_6O_4Sb$ %: C 49.07, H 2.34. Found: C 49.43, H 2.53. IR (nujol, cm^{-1}): $\nu(C-O)$ 1255, 1275, and 1290; $\nu(C-O-C)$ 1030; $\nu(C-Cl)$ 900; $\nu(Sb-O)$ 690; $\nu(Sb-Ph)$ 450. 1H NMR ($CDCl_3$), δ , ppm: 7.26–7.81 (m, 15H, aromatic).

Method 2. The synthesis and the product isolation of **2** were carried out similarly to the synthesis 3.2.1, method 2 for **1**. Thus, the reaction of triphenylantimony dichloride (0.42 g, 1 mmol) and perchloroxanthrenequinone-2,3 (0.42 g, 1 mmol) with the thallium amalgam yielded 0.59 g (76%) of yellow crystals.

3.2.3. 4-(2-Methyl-5-tert-butyl-cyclohexadien-1,5-dion-3,4-yl)-(3-methyl-6-tert-butyl-catecho-lato) triphenylantimony(V) $Ph_3Sb(Cat-Q)$ (**3**)

The synthesis and the product isolation were carried out similarly to the synthesis 3.2.1, method 1 for **1**. Thus, the reaction of triphenylantimony (0.79 g, 2.25 mmol) and 4,4'-di-(3-methyl-6-tert-butyl-*o*-benzoquinone) (0.80 g, 2.25 mmol) yielded 1.49 g (94%) of brownish red crystals; m.p. 200–201 °C. Anal. Calc. for $C_{40}H_{41}SbO_4$ %: C, 69.33; H, 6.02; Sb 16.16; Found: C, 68.97; H, 5.64; Sb 15.99; IR (nujol, cm^{-1}): $\nu(C=O)$ 1630, 1655, 1675, and 1680; $\nu(C-O)$ 1260, 1330; $\nu(Sb-O)$ 690; $\nu(Sb-Ph)$ 450. 1H NMR ($CDCl_3$), δ , ppm: 1.22 (s, 9H, Bu^t); 1.43 (s, 9H, Bu^{t'}); 1.82 (s, 3H, Me); 2.23 (s, 3H, Me'); 6.46 (s, 1H, C₆H₁); 6.79 (s, 1H, C₆H₁); 7.46–7.84 (m, 15H, aromatic).

3.2.4. 4,4'-Di-[(3-methyl-6-tert-butyl-catecholato) triphenylantimony(V)] $Ph_3Sb(Cat-Cat)SbPh_3$ (**4**)

Synthesis and product isolation were carried out similarly to the synthesis 3.2.1, method 1 for **1**. Thus, the reaction of triphenylantimony (1.59 g, 4.5 mmol) and 4,4'-di-(3-methyl-6-tert-butyl-*o*-benzoquinone) (0.80 g, 2.25 mmol) yielded 2.3 g (97%) of yellow crystals; m.p. 202 °C. The recrystallization from CH_2Cl_2 -hexane solution yielded crystals suitable for X-ray analysis; IR (nujol, cm^{-1}): $\nu(C-O)$ 1250 and 1265; $\nu(Sb-O)$ 690; $\nu(Sb-Ph)$ 450. 1H NMR ($CDCl_3$), δ , ppm: 1.43 (s, 18H, Bu^t); 2.13 (s, 6H, Me); 6.54 (s, 2H, C₆H₁); 7.43–7.86 (m, 30H, aromatic).

3.3. X-ray diffraction studies

Suitable crystals for X-ray diffraction were prepared by prolonged crystallization from toluene solution for **1** and **2** and from CH_2Cl_2 -hexane solution for **4**.

Intensity data were collected on a Smart Apex diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) in the φ - ω scan mode ($\omega = 0.3^\circ$, 10 s on each frame). Absorption corrections were made

by SADABS program [18]. The structures were solved by direct methods and refined on F^2 by full matrix least squares using SHELXTL [19]. All non-hydrogen atoms were refined anisotropically. The H atoms in complexes **1**, **2** (only for solvate molecule) and **4** and were placed in calculated positions and refined in the “riding-model” ($U_{iso}(H) = 1.2U_{iso}(\text{carbon}) \text{ \AA}^2$ for aromatic hydrogen and $1.5U_{iso}(\text{carbon}) \text{ \AA}^2$ for alkyl hydrogen), and in complex **2** were located from Fourier synthesis and refined isotropically. Table 1 summarizes the crystal data and some details of the data collection and refinement for **1**, **2** and **4**. Selected bond distances and angles for molecules of **1**, **2** and **4** are given in Tables 2–4, respectively.

4. Conclusions

The new catecholate complexes triphenyl(3,6-di-*tert*-butylcatecholato)antimony(V) $Ph_3Sb(3,6-DBCat)$, triphenyl(perchloroxanthrenecatecholato)antimony(V) $Ph_3Sb(O^XCatCl)$ and 4,4'-di-[(3-methyl-6-*tert*-butylcatecholato)triphenylantimony(V)] $Ph_3Sb(Cat-Cat)SbPh_3$ were synthesized by the convenient oxidative addition reaction with the high yields. We obtained 4-(2-methyl-5-*tert*-butyl-cyclohexadien-1,5-dion-3,4-yl)-(3-methyl-6-*tert*-butyl-catecholato)triphenylantimony(V) $Ph_3Sb(Cat-Q)$ by the same reaction. The more interesting is complex **3** which can be used as a ligand in the synthesis of new *o*-quinonato heterometal complexes.

5. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 249948 for **1**, 249949 for **2** and 249950 for **4**. Copies of this data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; email: deposit@ccdc.cam.ac.uk).

Acknowledgements

We are grateful to the Russian Foundation for Basic Research (Grant 04-03-32409) and Russian President Grant supporting scientific schools (Grants 1649.2003.3, 1652.2003.3) for financial support of this work. Spectroscopic investigations were carried out in the Analytical Centre of IMOC RAS.

References

- [1] M. Hall, D.B. Sowerby, J. Am. Chem. Soc. 102/2 (1980) 628–632.
- [2] R.R. Holmes, R.O. Day, V. Chandrasekhar, J.M. Holmes, Inorg. Chem. 26 (1987) 157–163.

- [3] R.R. Holmes, R.O. Day, V. Chandrasekhar, J.M. Holmes, *Inorg. Chem.* 26 (1987) 163–168.
- [4] Z. Tian, D.G. Tuck, *J. Chem. Soc., Dalton Trans.* (1993) 1381–1385.
- [5] G.K. Fukin, L.N. Zakharov, G.A. Domrachev, A.U. Fedorov, S.N. Ziburdaeva, V.A. Dodonov, *Russ. Chem. Bull.* 9 (1999) 1744–1753.
- [6] M.N. Gibbons, M.J. Begley, A.J. Blake, D.B. Sowerby, *J. Chem. Soc., Dalton Trans.* (1997) 2419–2425.
- [7] V.A. Muraev, G.A. Abakumov, G.A. Razuvaev, *Dokl. Akad. Nauk SSSR* 217 (1974) 1083–1086.
- [8] L.G. Abakumova, VI Fechem conference on organometallic chemistry. Riga 1985. *Book of Abstracts* (1985) 185.
- [9] P.A. Wicklund, L.S. Beckmann, D.G. Brown, *Inorg. Chem.* 15 (1976) 1996–1997.
- [10] C.G. Pierpont, R.M. Buchanan, *Coord. Chem. Rev.* 38 (1981) 45–87.
- [11] O. Carugo, B. Castellani, K. Djinovic, M. Rizzi, *J. Chem. Soc., Dalton Trans.* 5 (1992) 837–841.
- [12] S.S. Batsanov, *Russ. J. Inorg. Chem.* 36 (1991) 3015.
- [13] K.A. Kocheshkov, A.P. Skoldinov, N.N. Zemlyanskii, *Methods of Elementorganic Chemistry Stibium and Bismuth*, Nauka, Moscow, 1976.
- [14] Ye.G. Rozantsev, V.D. Sholle, *The Organic Chemistry of Free Radicals*, Chimia, Moscow, 1979.
- [15] L.G. Abakumova, L.V. Lobanov, G.A. Abakumov, *Izv. Akad. Nauk SSSR, Ser. Khim.* (1978) 204.
- [16] G.A. Abakumov, V.I. Nevodchikov, N.O. Druzhkov, V.K. Cherkasov, L.N. Zakharov, *Russ. Chem. Bull.* 4 (1997) 804–809.
- [17] D.D. Perrin, W.L.F. Armarego, D.R. Perrin, *Purification of Laboratory Chemicals*, Pergamon, Oxford, 1980.
- [18] G.M. Sheldrick, *SADABS v.2.01*, Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS, Madison, Wisconsin, USA, 1998a.
- [19] G.M. Sheldrick, *SHELXTL v. 6.12*, Structure Determination Software Suite, Bruker AXS, Madison, Wisconsin, USA, 2000.