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New organoselenium(II) derivatives containing Se-antimony bonds

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New organoantimony(III) selenolates, $RSb[Se\{C_6H_4(CH_2NMe_2)\text{-}2\}]_2$ [R = $(Me_3Si)_2CH$ (**1**), Me_3CCH_2 (**2**), Ph (**3**)] were prepared and characterized by mass spectrometry and NMR (^1H, ^{13}C) NMR spectroscopy. On the basis of the NMR data, a structure with nitrogen atoms of the pending arms coordinated to the metal centre was proposed.

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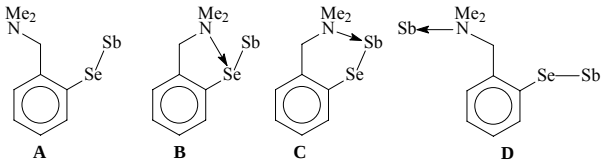
1. Introduction

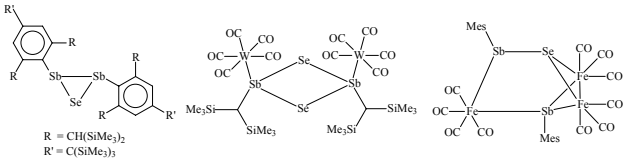
Metal and non-metal chalcogenolates have attracted an increased interest in last years due to their suitability to be used as single source precursors for CVD processes.[1-4] Especially Group 15 derivatives are excellent candidates for applications in electronics industry, including semiconductors, optical or electro-active materials.[5] However, the derivatives of heavier chalcogens were less studied in comparison with sulfur based complexes.

This paper describes some attempts made to obtain new antimony selenolates in order to investigate the potential of organic ligands with pendant arms to stabilize low oxidation states of metals. At least theoretically, there are various coordination patterns (Scheme 1). The pendant arm might be twisted as far as possible from both the selenium and the antimony centres (structure A) and in this case it will behave just as a sterically demanding group. The much more probable alternatives are that the nitrogen atom of the pendant arm remains coordinated to the selenium centre (structure B – five-membered SeC_3N chelate ring) or coordinates the antimony atom (structure C – six-membered $SbSeC_3N$ chelate ring), as observed in most of the metal compounds described in literature. Another possibility would be a structure in which the pendant arm is bridging two antimony centres (structure D).



Scheme 1

Relatively few organoselenium derivatives containing selenium-antimony bonds were described so far. Most of them are adducts obtained using neutral organoselenium ligands (selenoethers [6]). The molecular structures have been established by single-crystal X-ray diffraction for few inorganic antimony(III) compounds.[5, 7-10] On the other hand, only three organoantimony compounds with Sb-Se bonds were described (Scheme 2):[11-13]



Scheme 2

The scarce literature data on organoantimony selenolates is mainly due to the low stability of this type of compounds and therefore we decided to investigate the possibility to increase their stability using organoselenolato groups containing organic ligands with pendant arms.

2. Experimental

Materials and procedures

All manipulations were carried out under inert atmosphere (argon), using Schlenk techniques. Solvents were dried and distilled prior to use. The starting materials were prepared according to literature methods: $[2\text{-}(Me_2NCH_2)C_6H_4]_2Se_2$, [14] $[(Me_3Si)_2CHSb]_3$, [15] $(Me_3CCH_2Sb)_5$, [16] $PhSbCl_2$ [17]. Room-temperature ^1H and ^{13}C spectra for **1** and **2** (in dry C_6D_6) were recorded at room temperature on a BRUKER DPX 200 instrument operating at 200 and 50.3 MHz, respectively. Abbreviations used in multiplicities are: s, singlet; d, doublet; dd, doublet of doublets; ddd, doublet of doublet of doublets; m, multiplet. Mass spectra were recorded on a FINNIGAN MAT 8200 spectrometer.

Preparation of [bis(trimethylsilyl)methyl]antimony(III) bis[{2-(dimethylaminomethyl)phenyl}selenolate(II)], $(Me_3Si)_2CHSb[Se\{C_6H_4(CH_2NMe_2)\text{-}2\}]_2$ (1)

A solution of $[(Me_3Si)_2CHSb]_3$ (0.22 g, 0.26 mmol) in 20 mL petroleum ether was added dropwise to a solution of $[2\text{-}(Me_2NCH_2)C_6H_4]_2Se_2$ (0.33 g, 0.77 mmol) in 20 mL petroleum ether, under argon. The reaction mixture was stirred at reflux for 1 h when the product precipitated as a brown solid. Filtration and washing with hexane gave 0.3 g (62%) of **1**.

MS [DCI, NH_3; *m/z* (%)]: 709 (100) $(Me_3Si)_2CHSb[Se\{C_6H_4(CH_2NMe_2)\text{-}2\}]_2^+$, 494 (87) $[(Me_3Si)_2CHSbSe\{C_6H_4(CH_2NMe_2)\text{-}2\}^+]$, 214 (26) $[\{2\text{-}(Me_2NCH_2)C_6H_4\}Se^+]$, 134 (14) $[2\text{-}(Me_2NCH_2)C_6H_4^+]$.

0.36s [18H, $Si(CH_3)_3$], 0.76s (1H, Sb-C*H*), 2.06s (12H, N-CH_3), AB spin system with A: 3.28, B: 3.84 (4H, -CH_2-, $^2J_{HH}$ 12.6 Hz), 6.84ddd (2H, -C_6H_4-, H_4, $^3J_{HH}$ 7.5, $^4J_{HH}$ 1.7 Hz), 6.99ddd (2H, -C_6H_4-, H_5, $^3J_{HH}$ 7.5, $^4J_{HH}$ 1.4 Hz), 7.21dd (2H, -C_6H_4-, H_3, $^3J_{HH}$ 7.5 Hz, $^4J_{HH}$ 1.5 Hz), 7.65dd (2H, -C_6H_4-, H_6, $^3J_{HH}$ 7.6, $^4J_{HH}$ 1.4 Hz).

3.81s [$Si(CH_3)_3$], 14.69s (Sb-*C*H), 45.47s (N-*C*H_3), 65.67s (-*C*H_2-), 130.65s, 132.37s (-*C*$_6H_4$-, *C*H), 138.75s, 142.97s (-*C*$_6H_4$-, $C_{1,2}$); two of the aromatic *C*H resonances are overlapped by the C_6D_6 signal.

Generation of [2,2-(dimethyl)propyl]antimony(III) bis[{2-(dimethylaminomethyl)phenyl}selenolate(II)], $Me_3CCH_2Sb[Se\{C_6H_4(CH_2NMe_2)\text{-}2\}]_2$ (2)

A mixture of $(Me_3CCH_2Sb)_5$ (0.016 g, 0.016 mmol) and $[2\text{-}(Me_2NCH_2)C_6H_4]_2Se_2$ (0.034 g, 0.08 mmol) in C_6D_6 was sealed, under argon, in an NMR tube. The solution turned immediately to yellow and was heated for 1 h. After 2 h the ^1H NMR spectrum of the sample show the total transformation of the starting material. MS analysis were carried out on the C_6D_6 solution.

MS [DCI, NH_3; *m/z* (%)]: 621 (55) $Me_3CCH_2Sb[Se\{C_6H_4(CH_2NMe_2)\text{-}2\}]_2^+$, 406 (100) $[Me_3CCH_2SbSe\{C_6H_4(CH_2NMe_2)\text{-}2\}^+]$, 214 (50) $[\{2\text{-}(Me_2NCH_2)C_6H_4\}Se^+]$, 134 (18) $[2\text{-}(Me_2NCH_2)C_6H_4^+]$.

0.98s [9H, $C(CH_3)_3$], 2.03s (6H, N-CH_3), 2.31s (2H, Sb-CH_2), AB spin system with A: 3.46, B: 3.66 (4H, -CH_2-, $^2J_{HH}$ 12.5 Hz), 6.88ddd (2H, -C_6H_4-, H_4, $^3J_{HH}$ 7.4 Hz, $^4J_{HH}$ 1.7 Hz), 7.00ddd (2H, -C_6H_4-, H_5, $^3J_{HH}$ 7.3, $^4J_{HH}$ 1.4 Hz), 7.20dd (2H, -C_6H_4-, H_3, $^3J_{HH}$ 7.4, $^4J_{HH}$ 1.6 Hz), 7.83dd (2H, -C_6H_4-, H_6, $^3J_{HH}$ 7.5, $^4J_{HH}$ 1.4 Hz).

32.97s [*C*$(CH_3)_3$], 44.39s (Sb-*C*H_2), 45.48s (N-*C*H_3), 65.81s (-*C*H_2-), 127.32s, 127.90s, 130.70s, 132.19s (-*C*$_6H_4$-, *C*H), 138.53s, 142.68s (-*C*$_6H_4$-, $C_{1,2}$).

Preparation of phenylantimony(III) bis[{2-(dimethylaminomethyl)phenyl}selenolate(II)], $PhSb[Se\{C_6H_4(CH_2NMe_2)\text{-}2\}]_2$ (3)

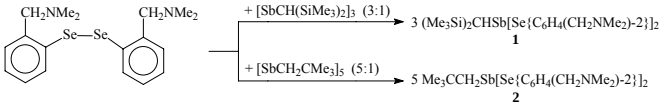
Elemental selenium (0.42 g, 5.32 mmol) was added to a solution of $[2\text{-}(Me_2NCH_2)C_6H_4]Li$ (0.75 g, 5.32 mmol) in 20 mL anhydrous diethyl ether and the reaction mixture was stirred for 2 h at room temperature, under argon. The resulting yellow solution was treated dropwise with a solution of $PhSbCl_2$ (0.72 g, 2.66 mmol) in 30 mL anhydrous diethyl ether. After stirring for additional 2 hours LiCl separated as a white precipitate and was filtered off. The yellow solution was concentrated under reduced pressure until **3** precipitated as a yellow solid. Recrystallization from methylene dichloride / n-hexane (1:5, v/v) gave 0.75 g (45%) of **3**. M.p. 184-186ºC.

MS [EI, 70 eV, 200ºC; *m/z* (%)]: 584 (15) $[M\text{-}NMe_2^+]$, 428 (25) $[\{2\text{-}(Me_2NCH_2)C_6H_4\}Se]_2^+$, 198 (97) $(PhSb^+)$, 154 (100) (Ph_2^+).

3. Results and discussion

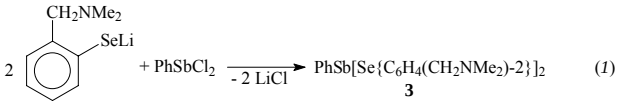
Synthesis and NMR scale reactions

Compounds **1** and **2** were generated directly in an NMR tube, using the redistribution reaction between $[2\text{-}(Me_2NCH_2)C_6H_4]_2Se_2$ and *cyclo*-$(SbR')_n$ [**1**, n = 3, R′ = $CH(SiMe_3)_2$; **2**, n = 5, R′ = CH_2CMe_3], in dry C_6D_6, according to Scheme 3. The yellow solution formed immediately was heated for 1 hour and then the NMR spectra were recorded. From the NMR data we concluded the total transformation of the starting material. Compound **1** was also prepared on a large scale and isolated as a brown crystaline product.



Scheme 3

Compound **3** was obtained using the *ortho*-lithiation procedure, *i.e.* selenium insertion into the C-Li bond of $[2\text{-}(Me_2NCH_2)C_6H_4]Li$ [18] (under argon, in THF), followed by the reaction of the *in situ* resulted $[2\text{-}(Me_2NCH_2)C_6H_4]SeLi$ with $PhSbCl_2$, in diethyl ether, at room temperature, according to eq. (*1*):



All three compounds were characterized by mass spectroscopy, while for compounds **1** and **2** multinuclear NMR studies were also performed.

Mass spectroscopic investigations of 1 - 3

The mass spectra of all three organoantimony(III) derivatives **1**-**3** are consistent with the formulation of the compounds. The DCI mass spectrum for compound **1** exhibits the molecular ion, $(Me_3Si)_2CHSb[Se\{C_6H_4(CH_2NMe_2)\text{-}2\}]_2^+$, as base peak [*m/z* 709 (100%]. For compound **2** the base peak was a fragment, *i.e.* $Me_3CCH_2SbSe\{C_6H_4(CH_2NMe_2)\text{-}2\}^+$ [*m/z*

406 (100%)], which resulted by elimination of a $Se[C_6H_4(CH_2NMe_2)$-2] unit. The molecular ion, $(Me_3Si)_2CHSb[Se\{C_6H_4(CH_2NMe_2)-2\}]_2^+$ [*m/z* 621 (55%], was also observed as a highly intense peak.

By contrast, in the EI mass spectrum of compound **3** only fragment ions containing either antimony or selenium were observed.

NMR spectroscopic investigations of 1 and 2

The NMR spectra for compounds **1** and **2** were recorded in C_6D_6, at room temperature.

The ^{1}H spectrum for compound **1** is shown in Figures 1 and 2. They exhibit the expected resonances for both organic groups bonded to selenium and antimony atoms. The aliphatic region of the ^{1}H NMR spectrum (Figure 1) shows two singlet resonances corresponding to the protons of the bis(trimethylsilyl)methyl group attached to antimony: δ 0.36 ppm for C*H*$_3$-Si and δ 0.76 ppm for C*H*-Sb, respectively. For the organic group attached to selenium, in addition to a singlet resonance for the NMe_2 group (δ 2.06 ppm), an AB system is observed for the methylene protons, -C*H*$_2$-N: δ_A 3.28, δ_B 3.84 ppm ($^2J_{HH}$ 12.6 Hz). This pattern is consistent with the coordination of the nitrogen atom from the pending arm either to the selenium or to the antimony atom.

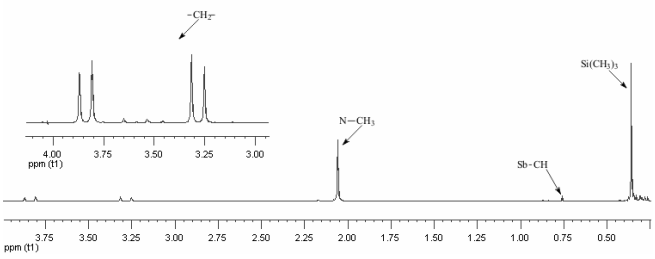


Fig. 1. The aliphatic region of the ^{1}H NMR spectrum of $(Me_3Si)_2CHSb[Se\{C_6H_4(CH_2NMe_2)-2\}]_2$ (1), in C_6D_6.

Four, well-separated, resonances were observed in the aromatic region of the ^{1}H NMR spectrum of **1** (Fig. 2). On the basis of multiplicity, the doublet of doublet of doublets were assigned to H_4 / H_5 protons, while the doublet of doublets were assigned to H_3 / H_6 aromatic protons of the 2-$(Me_2NCH_2)C_6H_4$ group. To distinguish between H_4 / H_5 and H_3 / H_6 protons, respectively, *i.e.* for an unequivocally assignment of the resonance signals, a simulation of the aromatic region was performed using the *g*NMR program (Fig. 2).

The ^{13}C NMR spectrum of compound **1** exhibits the expected four resonances for the aliphatic carbon atoms, which were assigned by comparison with the spectra of the starting materials. In the aromatic region only four resonances could be observed for the carbon atoms of the 2-$(Me_2NCH_2)C_6H_4$ group, other two resonances for *C*H carbons being overlapped by the solvent (C_6D_6) signal.

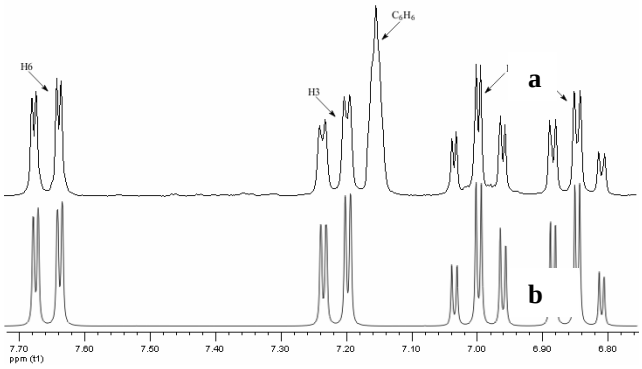


Fig. 2. Aromatic region of the ^{1}H NMR spectrum of $(Me_3Si)_2CHSb[Se\{C_6H_4(CH_2NMe_2)-2\}]_2$ (1): (a) experimental (C_6D_6, 200 MHz, 20 ºC), and (b) simulated on the basis of the following parameters:

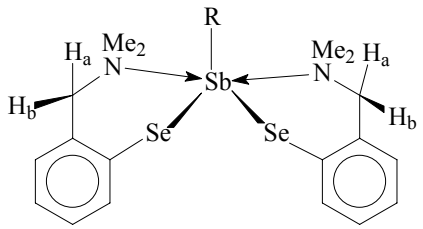
δ 6.845 ppm [ddd, 1H, *H*-4, $^3J_{HH}$ 7.5 (H-5), $^3J_{HH}$ 7.6 (H-3), $^4J_{HH}$ 1.5 (H-6) Hz];
δ 6.991 ppm [ddd, 1H, *H*-5, $^3J_{HH}$ 7.5 (H-6), $^3J_{HH}$ 7.5 (H-4), $^4J_{HH}$ 1.4 (H-3) Hz];
δ 7.211 ppm [ddd, 1H, *H*-3, $^3J_{HH}$ 7.6 (H-4), $^4J_{HH}$ 1.4 (H-5), $^5J_{HH}$ 0.3 (H-6) Hz];
δ 7.653 ppm [ddd, 1H, *H*-6, $^3J_{HH}$ 7.5 (H-5), $^4J_{HH}$ 1.5 (H-4), $^5J_{HH}$ 0.3 (H-3) Hz].

The ^{1}H and ^{13}C NMR spectra of compound **2** contain the expected resonances. With respect to the 2-$(Me_2NCH_2)C_6H_4$ group they are very similar to those of compound **1**. An AB spin system is observed for the methylene protons, -C*H*$_2$-N: δ_A 3.46, δ_B 3.66 ppm ($^2J_{HH}$ 12.5 Hz). The assignment of the resonances in the aromatic region of the ^{1}H NMR spectrum was based on a simulation using the *g*NMR program, on the basis of the following parameters:

δ 6.888 ppm [ddd, 1H, *H*-4, $^3J_{HH}$ 7.4 (H-5), $^3J_{HH}$ 7.5 (H-3), $^4J_{HH}$ 1.6 (H-6) Hz];
δ 7.001 ppm [ddd, 1H, *H*-5, $^3J_{HH}$ 7.5 (H-6), $^3J_{HH}$ 7.4 (H-4), $^4J_{HH}$ 1.4 (H-3) Hz];
δ 7.204 ppm [ddd, 1H, *H*-3, $^3J_{HH}$ 7.5 (H-4), $^4J_{HH}$ 1.4 (H-5), $^5J_{HH}$ 0.2 (H-6) Hz];
δ 7.834 ppm [ddd, 1H, *H*-6, $^3J_{HH}$ 7.5 (H-5), $^4J_{HH}$ 1.6 (H-4), $^5J_{HH}$ 0.2 (H-3) Hz].

In the ^{13}C NMR spectrum of compound **2** all six resonances corresponding to the aromatic carbon atoms could be observed.

On the basis of the NMR data in solution the structure of types **A** and **D**, as well as rapid equilibria can be excluded. From the remaining structures, **B** and **C**, the latter can be excluded because it does not correspond to the appearance of the AB spin system for the CH_2 groups. On the basis of the ^{1}H NMR data the structural type **C** is most likely. The proposed structure is shown in Scheme 4.



Scheme 4

On the NMR time scale the six membered heterocycles can be considered as planar. The hydrogen atoms of the CH_2 group are not equivalent, H_a being oriented on the same side with the R group on antimony and H_b on the opposite side. Therefor an AB spin system for the methylene protons results. The equivalence of the Me_2N protons results from a rapid on nitrogen inversion and ring opening processes.

4. Conclusions

With the synthesis of **1** – **3** new potential precursors for CVD processes and electronic applications with a Sb/Se ratio 1 : 2 were obtained.

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