Neutral and Dianionic Organoantimony(III) Dithiolene Complexes: Syntheses, X-ray Crystal Structures, and Unexpected Reactivity

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The new neutral PhSb(dmid) (dmid^{2-} = 4,5-dithiolato-1,3-dithiol-2-one) complex has been synthesized upon reaction of deprotected 1,3,4,6-tetrathiapentalene-2,5-dione with dichlorophenylstibine. Single-crystal X-ray structure determination shows an original three-dimensional network in the solid state, via Sb- - -O and Sb- - -S secondary interactions, based on an octagonal "Sb_4S_4" motif. Not only PhSb(dmid) but also PhSb(dmit) (dmit^{2-} = 4,5-dithiolato-1,3-dithiole-2-thione) reacts with a second 1 equiv of dithiolate to give a series of highly reactive dianionic complexes, unknown so far. One of these complexes, $[Me_4N]_2[PhSb(dmid)_2]$, was structurally characterized by single-crystal X-ray measurements. Both dithiolene ligands, lying in the equatorial plane of a distorted octahedron, are unsymmetrically coordinated, with two Sb−S distances much longer than the other two. These dianionic species reacted with 1 equiv of $PhSbCl_2$ to give, unexpectedly, a series of Sb(V) $[Ph_2Sb(dithiolene)_2]^-$ complexes. The same compounds were obtained directly upon slow addition of 1 equiv of $PhSbCl_2$ on the corresponding dithiolate suspensions. This demonstrates that dianionic $[PhSb^{III}(dithiolene)_2]^{2-}$ species are key intermediates in the synthesis of $[Ph_2Sb^{V}(dithiolene)_2]^-$ salts. The single-crystal X-ray structure determination of the tetraethylammonium salts of $[Ph_2Sb(dmid)_2]^-$, $[Ph_2Sb(dmit)_2]^-$, and $[Ph_2Sb(dmid)(dmit)]^-$ show a distorted-octahedral coordination geometry for the Sb center with a cis configuration of the phenyl groups. This is preserved also in solution, as established by ^{13}C NMR. Using the same technique, combined with ^{1}H NMR, in a scrambling experiment, a fast dithiolene exchange has been emphasized. In the case of the $[Ph_2Sb(dmid)_2]^-$ salt, two polymorphs, with different folding angles along the S- - -S hinge, were crystallized.

Introduction

The coordination chemistry of dithiolene ligands has been extensively and increasingly studied over the past decade.[1] The interest in using this class of ligands relates on their "noninnocence" on one hand, since in dithiolene-based transition-metal complexes the HOMO has mainly a ligand character, and their capacity to establish short intermolecular S- - -S interactions in the solid state on the other hand. Both features are very important for the synthesis of crystalline molecular materials with conducting and magnetic properties. Indeed, the redox behavior of dithiolene complexes, determined by the nature and relative position of the frontier orbitals, can be finely tuned by changing either the substituents on the dithiolene or the coordinated metallic center, leading to the stabilization of complexes in several oxidation states. This specific electrochemical behavior has found recently a nice application in solution, in the catalytic separation and purification of olefins.[2] In the solid state, besides the intrinsic electronic properties of the molecular entities, all the intermolecular interactions occurring in the crystal ultimately determine the collective properties such as conductivity and magnetism. For example, in the crystal structure of the mixed-valence superconducting salt $[Me_4N][Ni(dmit)_2]_2$ (dmit^{2-} = 4,5-dithiolato-1,3-dithiole-2-thione), short intermolecular S- - -S contacts (3.49 Å) ensure the 2D character of the conductor,[3] or, more recently, a single-component molecular metal, $Ni(tmdt)_2$ (tmdt = trimethylenetetrathiafulvalenedithiolate), synthesized by Kobayashi et al. shows a 3D solid-state organization of the molecules due to short S- - -S intermolecular interactions.[4]

If another heavy atom (X) of groups 14−17 is present in the structure of sulfur-rich molecules such as dithiolenes, one can expect additional intermolecular inter-

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actions of X- - -S or X- - -X type, which could eventually overcome the S- - -S interactions and thus drive the solid-state organization of these compounds. This is particularly well illustrated in the case of open antimony sulfide frameworks,[5] in which intermolecular Sb- - -S and Sb- - -Sb contacts lead to a huge variety of structures. Therefore, the introduction of antimony in dithiolenes such as dmit and dmid (dmid^{2-} = 4,5-dithiolato-1,3-dithiol-2-one), which can be also seen as "half-tetrathiafulvalenes" (TTF), seemed to us particularly interesting from structural, coordination, and materials science points of view. In this respect, our recent results[6] concerning the first organoantimony(III) dithiolene complex, PhSb(dmit), confirmed our expectations, since the cooperativity between S- - -S and Sb- - -S intermolecular contacts led to the formation of an original three-dimensional network in the solid state. Moreover, we could clearly emphasize the existence of two reversible single-crystal phase transitions involving the coordination sphere of antimony, thus showing its flexibility. We describe here the synthesis and structural characterization of PhSb(dmid) and investigate its reactivity together with that of PhSb(dmit). The interest in synthesizing the former complex directly follows from the crystal structure of PhSb(dmit), in which we observed that all the secondary short Sb- - -S contacts involved the C=S sulfur atoms: hence, the idea of replacing C=S by C=O in the ligand structure. One can notice that the same interactions were present in the structure of previously described monoanionic salts [Sb(dmit)$_2$]$^-$.[7]

Experimental Section

General Comments. The reactions were carried out under an inert atmosphere of nitrogen by using Schlenk techniques. Dry toluene and hexane were obtained by distillation over Na and dry CH_2Cl_2 and MeCN by distillation over P_2O_5, and THF was distilled over sodium and benzophenone. Nuclear magnetic resonance spectra were recorded for compounds **2**, **4**, and **8**−**10** on a Bruker ARX 400 spectrometer operating at 400.13 MHz for ^{1}H and 100.62 MHz for ^{13}C and for compounds **5**−**7** on a Bruker Avance DRX 500 spectrometer operating at 500.04 MHz for ^{1}H and 125.75 MHz for ^{13}C. Chemical shifts are expressed in parts per million (ppm) downfield from external TMS. The following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad. Mass spectrometry was performed on an HP 5989A spectrometer in the EI mode, with an ionization energy of 70 eV. Infrared spectroscopy was measured on a Nicolet FTIR 20 SXC spectrometer. The following abbreviations are used: s, strong; m, medium. Elemental analyses were performed by the "Service d'Analyse du CNRS" at Gif/Yvette, France. 1,3,4,6-Tetrathiapentalene-2,5-dione[8] (**1**), 4,5-bis((2-cyanoethyl)thio)-1,3-dithiole-2-thione[9] (**3**), and phenyldichlorostibine[10] were prepared according to published procedures.

Synthesis of Phenyl(1,3-dithiol-2-one-4,5-dithiolato)antimony(III) (2). In a Schlenk tube containing 1,3,4,6-tetrathiapentalene-2,5-dione (**1**; 2 g, 9.6 mmol) in 70 mL of THF, a solution of Me_4NOH (7 g, 25 wt % in MeOH, 19.2 mmol) in 10 mL of THF was added under magnetic stirring. A yellow precipitate suddenly appeared, corresponding to the formation of $(Me_4N)_2$(dmid). After 30 min of stirring at room temperature, dichlorophenylstibine (2.6 g, 9.6 mmol) in 10 mL of THF was rapidly added. The solution became orange, and a cream-colored precipitate of tetramethylammonium chloride was formed. The suspension was stirred for 1 h and then filtered through Celite. After evaporation of solvent, the resulting oil was dissolved in a minimum amount of toluene and then rapidly chromatographed with toluene through a short silica gel column. After removal of solvent under vacuum, addition of a small volume of THF, precipitation with pentane, filtration, and drying on a vacuum line, complex **2** was recovered as a yellow solid. Yield: 1.7 g (47%). Single crystals for X-ray analysis were grown by slow diffusion of hexane into a solution of **2** in toluene.

^{1}H NMR (δ, THF-d_8): 7.31−7.41 (m, 3H, H *para* and *meta*), 7.79 (dd, 2H, ^3J = 8.0 Hz, ^4J = 0.7 Hz, H *ortho*). ^{13}C NMR (δ, THF-d_8): 116.6 (s, C=C), 127.1 (s, CH *meta*), 128.1 (s, CH *para*), 132.0 (s, CH *ortho*), 146.6 (s, C *ipso*), 192.0 (s, C=O). IR (KBr, cm^{-1}): 1661 (s, C=O), 1586 (s, C=O), 1480 (m, C=C), 894 (m, C−S), 727 (m, C_6H_5), 690 (m, C_6H_5), 464 (m, C_6H_5). MS (EI) (*m/z* (ion, relative intensity)): 379, 377 (M$^+$, 80), 351, 349 ((M − C=O)$^+$, 12), 200, 198 (PhSb$^+$, 100). Anal. Calcd for $C_9H_5OS_4Sb$: C, 28.51; H, 1.33. Found: C, 29.17; H, 1.33.

Synthesis of Phenyl(1,3-dithiole-2-thione-4,5-dithiolato)antimony(III) (4). A solution of 4,5-bis((2-cyanoethyl)thio)-1,3-dithiole-2-thione (**3′**; 2 g, 6.58 mmol) in 40 mL of THF was treated with a solution of Me_4NOH (4.8 g, 25 wt % in MeOH, 13.2 mmol) in 10 mL of THF. A blue precipitate of $(Me_4N)_2$(dmit) was formed within a few minutes and after 30 min of stirring dichlorophenylstibine (1.8 g, 6.6 mmol) in 10 mL THF was rapidly added. The resulting deep orange solution was stirred for 2 h and then filtered through Celite in order to remove the precipitated Me_4NCl and eluted through a short silica gel column with THF. After evaporation of almost all the solvent, precipitation upon addition of pentane, filtration on a glass frit, washing of the resulting powder with methanol and then with pentane and finally drying under vacuum, **4** was recovered as a deep red solid. Yield: 1.9 g (73%). All the characterizations were in agreement with the published data.[6]

Synthesis of the Bis(tetramethylammonium) Salt of Phenylbis(1,3-dithiol-2-one-4,5-dithiolato)antimony(III) (5). Tetramethylammonium hydroxide (0.2 g, 25 wt % in MeOH, 0.54 mmol) in 5 mL of THF was added, with magnetic stirring, in a Schlenk tube containing a solution of **1** (0.055 g, 0.27 mmol) in 5 mL of THF. A yellow precipitate of $(Me_4N)_2$(dmid) rapidly appeared, and after 30 min of stirring a solution of PhSb(dmid) (**2**; 0.1 g, 0.27 mmol) in 5 mL of THF was added. An orange solid started to precipitate, and then the resulting suspension was stirred for a further 30 min. Filtration over a glass frit under an inert atmosphere, followed by washing with THF and drying under vacuum, yielded **5** as an orange solid highly sensitive to oxygen. Yield: 0.165 g (88%). Suitable crystals for X-ray analysis have been grown from a saturated solution of dianion **5** in acetonitrile at −20 °C.

^{1}H NMR (δ, CD_3CN): 3.06 (s, 24H, CH_3), 7.18−7.21 (m, 1H, H *para*), 7.26 (t, 2H, ^3J = 7.1 Hz, H *meta*), 8.11 (d, 2H, ^3J = 7.1 Hz, H *ortho*). ^{13}C NMR (δ, CD_3CN): 56.8 (t, ^1J = 3.9 Hz, CH_3), 122.6 (s, C=C), 128.7 (s, CH *para*), 128.9 (s, CH *meta*), 137.1 (s, CH *ortho*), 155.0 (s, C *ipso*), 196.5 (s, C=O).

Synthesis of the Bis(tetramethylammonium) Salt of Phenylbis(1,3-dithiole-2-thione-4,5-dithiolato)antimony(III) (6). To a solution of **3** (0.25 g, 0.82 mmol) in 15 mL of THF was added tetramethylammonium hydroxide (0.6 g, 25 wt % in MeOH, 1.64 mmol) in 5 mL of THF. After 30 min of

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stirring a solution of PhSb(dmit) (**4**; 0.32 g, 0.82 mmol) in 10 mL of THF was syringed in, and the blue precipitate of $(Me_4N)_2$(dmit) rapidly dissolved. A deep red color appeared, and the solution was stirred for a further 2 h. Then, precipitation with hexane, filtration on a glass frit under an inert atmosphere, and drying on a vacuum line allowed the isolation of **6** as a red-purple solid highly sensitive to oxygen. Yield: 0.56 g (91%).

^{1}H NMR (δ, CD_3CN): 3.06 (s, 24H, CH_3), 7.21−7.25 (m, 1H, H *para*), 7.30 (t, 2H, $^3J = 7.2$ Hz, H *meta*), 8.05 (d, 2H, $^3J = 7.2$ Hz, H *ortho*). ^{13}C NMR (δ, CD_3CN): 56.8 (t, $^1J = 3.9$ Hz, CH_3), 129.2 (s, CH *para*), 129.3 (s, CH-*meta*), 136.8 (s, CH *ortho*), 137.1 (s, C=C), 154.0 (s, C *ipso*), 213.9 (s, C=S).

Synthesis of the Bis(tetramethylammonium) Salt of Phenyl(1,3-dithiole-2-thione-4,5-dithiolato)(1,3-dithiol-2-one-4,5-dithiolato)antimony(III) (7). In a Schlenk tube containing **1** (0.105 g, 0.51 mmol) in 10 mL of THF, Me_4NOH (0.37 g, 25 wt % in MeOH, 1.02 mmol) in 5 mL of THF was added. Rapid formation of $(Me_4N)_2$(dmid) occurred, and after 30 min of stirring, a solution of PhSb(dmit) (**4**; 0.2 g, 0.51 mmol) in 20 mL THF was syringed in. The red suspension thus obtained was stirred for 2 h, and then hexane was added in order to precipitate all the dianionic salt. The mixed bis(dithiolene) complex **7** was recovered as a red solid, sensitive to oxygen, after filtration, washing with hexane, and drying under vacuum. Yield: 0.33 g (90%).

^{1}H NMR (δ, CD_3CN): 3.06 (s, 24H, CH_3), 7.22−7.23 (m, 1H, H *para*), 7.28 (t, 2H, $^3J = 7.2$ Hz, H *meta*), 8.07 (d, 2H, $^3J = 7.2$ Hz, H *ortho*). ^{13}C NMR (δ, CD_3CN): 56.8 (t, $^1J = 3.9$ Hz, CH_3), 122.1 (s, C=C), 128.9 (s, CH *para*), 129.1 (s, CH *meta*), 136.9 (s, CH *ortho*), 138.2 (s, C=C), 154.4 (s, C *ipso*), 196.2 (s, C=O), 213.7 (s, C=S).

Synthesis of the Tetraethylammonium Salt of Diphenylbis(1,3-dithiol-2-one-4,5-dithiolato)antimony(V) (8). Method A. To a solution of **1** (0.5 g, 2.4 mmol) in 30 mL of THF was added Et_4NOH (2.83 g, 25 wt % in MeOH, 4.8 mmol) in 10 mL of THF with magnetic stirring. An orange suspension was rapidly formed, and after 30 min of stirring, $PhSbCl_2$ (0.33 g, 1.2 mmol) in 5 mL of THF was added in one portion. Formation of the bis(dithiolate) was considered to be complete after 2 h of stirring, and then the second 1 equiv of $PhSbCl_2$ (0.33 g, 1.2 mmol) in 5 mL of THF was slowly added. The red suspension thus formed was stirred for a further 3 h and then filtered through Celite. Fast elution through neutral alumina with ethyl acetate (AcOEt), evaporation of almost all the solvent, precipitation with pentane, filtration, and drying under vacuum yielded **8** as a red air-stable solid. Yield: 0.3 g (33%).

Method B. The same conditions were employed as in method A to generate the dithiolate. Then a solution of PhSb(dmid) (**2**; 0.91 g, 2.4 mmol) in 10 mL of THF was syringed in and the resulting orange-red suspension was stirred for a further 2 h. After this period $PhSbCl_2$ (0.65 g, 2.4 mmol) in 10 mL of THF was added dropwise and the color rapidly changed to red upon addition. After 3 h of stirring the resulting mixture was worked up as in method A. Yield: 0.75 g (41%).

Suitable single crystals for X-ray analysis were grown by slow diffusion of hexane into a THF solution of **8** (monoclinic phase **8a**) or by cooling to −18 °C a THF−toluene solution of **8** (orthorhombic phase **8b**).

^{1}H NMR (δ, THF-d_8): 1.17 (t, 12H, $^3J = 7.2$ Hz, CH_3), 3.16 (q, 8H, $^3J = 7.2$ Hz, CH_2), 7.16−7.26 (m, 6H, H *para* and *meta*), 7.70 (dd, 4H, $^3J = 7.4$ Hz, $^4J = 1.47$ Hz, H *ortho*). ^{13}C NMR (δ, THF-d_8): 5.2 (s, CH_3), 50.6 (s, CH_2), 121.5 (s, C=C), 125.9 (s, CH *meta*), 127.0 (s, CH *para*), 128.1 (s, C=C), 131.3 (s, CH *ortho*), 151.4 (s, C *ipso*), 189.1 (s, C=O). IR (KBr, cm^{-1}): 1657 (s, C=O), 1607 (s, C=O), 1474 (m, C=C), 890 (m, C−S), 729 (m, C_6H_5), 688 (m, C_6H_5), 452 (m, C_6H_5). Anal. Calcd for $C_{26}H_{30}NO_2S_8Sb$: C, 40.73; H, 3.94. Found: C, 40.12; H, 4.09.

Synthesis of the Tetraethylammonium Salt of Diphenylbis(1,3-dithiole-2-thione-4,5-dithiolato)antimony(V) (9). NEt_4OH (1.94 g, 25 wt % in MeOH, 3.3 mmol) in 5 mL of THF was added in a Schlenk tube containing a solution of **3** (0.5 g, 1.65 mmol) in 15 mL of THF. A violet suspension rapidly formed, and after 30 min of stirring $PhSbCl_2$ (0.23 g, 0.83 mmol) in 5 mL of THF was added in one portion. The resulting red solution was stirred for 2 h, and after this period a second 1 equiv of $PhSbCl_2$ (0.23 g, 0.83 mmol) in 10 mL of THF was added dropwise. The mixture thus formed was stirred for 3 h, and then it was filtered first through Celite and second through a neutral alumina column with AcOEt as solvent. After evaporation, precipitation with pentane, filtration, and drying **9** was recovered as a red solid. Yield: 0.25 g (38%). Deep red crystals were obtained by slow diffusion of hexane into a solution of **9** in THF. ^{1}H NMR and IR spectra are in good agreement with already published data.[11] The ^{13}C NMR spectrum was not reported in ref 11; therefore, it is presented here.

^{13}C NMR (δ, CD_3CN): 7.1 (s, CH_3), 52.5 (s, CH_2), 128.5 (s, CH *meta*), 129.9 (s, CH *para*), 132.9 (s, CH *ortho*), 135.1 (s, C=C), 141.7 (s, C=C), 152.2 (s, C *ipso*), 212.0 (s, C=S). Anal. Calcd for $C_{26}H_{30}NS_{10}Sb$: C, 39.09; H, 3.78. Found: C, 38.27; H, 3.74.

Synthesis of the Tetraethylammonium Salt of Diphenyl(1,3-dithiole-2-thione-4,5-dithiolato)(1,3-dithiol-2-one-4,5-dithiolato)antimony(V) (10). To a solution of **1** (0.11 g, 0.5 mmol) in 10 mL of THF was added Et_4NOH (0.6 g 25 wt % in MeOH, 1 mmol) in 5 mL of THF. The orange suspension thus obtained was stirred for 30 min, and then a solution of PhSb(dmit) (**4**; 0.2 g, 0.5 mmol) in 10 mL of THF was added. The resulting solution, which became rose red upon addition, was stirred for a further 2 h. After this period $PhSbCl_2$ (0.14 g, 0.5 mmol) in 5 mL of THF was added dropwise and a color change to deep red was observed. Formation of **10** was assumed to be complete after 3 h of stirring, and then the mixture was filtered through Celite and chromatographed through neutral alumina with acetone as solvent. Removal of solvent, precipitation with pentane, and filtration on a glass frit allowed the isolation of **10** as a red solid. Yield: 0.15 g (38%). Single crystals were grown by diffusion of hexane into a THF solution of **10**.

^{1}H NMR (δ, THF-d_8): 1.23 (t, 12H, $^3J = 7.2$ Hz, CH_3), 3.20 (q, 8H, $^3J = 7.2$ Hz, CH_2), 7.19−7.24 (m, 6H, H *para* and *meta*), 7.69−7.73 (m, 4H, H *ortho*). ^{13}C NMR (δ, THF-d_8): 7.9 (s, CH_3), 53.3 (s, CH_2), 124.2 (s, C=C), 125.0 (s, C=C), 128.6 (s, CH *meta*), 128.7 (s, CH *meta*), 128.7 (s, CH *meta*), 128.8 (s, CH *meta*), 129.7 (s, CH *para*), 129.8 (s, CH *para*), 129.9 (s, CH *para*), 130.0 (s, CH *para*), 130.9 (s, C=C), 131.0 (s, C=C), 134.0 (s, CH *ortho*), 134.1 (s, CH *ortho*), 134.2 (s, CH *ortho*), 134.8 (s, C=C), 135.4 (s, C=C), 142.0 (s, C=C), 153.6 (s, C *ipso*), 154.0 (s, C *ipso*), 154.1 (s, C *ipso*), 154.5 (s, C *ipso*), 191.9 (s, C=O), 192.0 (s, C=O), 211.4 (s, C=S), 211.6 (s, C=S). IR (KBr, cm^{-1}): 1662 (s, C=O), 1610 (s, C=O), 1474 (m, C=C), 1425 (m, C=C), 1058 (s, C=S), 898 (m, C−S), 733 (m, C_6H_5), 690 (m, C_6H_5), 461 (m, C_6H_5). Anal. Calcd for $C_{26}H_{30}NOS_9Sb$: C, 39.89; H, 3.86. Found: C, 39.39; H, 3.91.

X-ray Crystallography. Details about data collection and solution refinement are given in Table 1. Data were collected on a Stoe-IPDS imaging plate system for all the compounds. The structure for **5** was solved by Patterson methods, and the other structures were solved by direct methods (SHELXS); all were refined (SHELXL-97)[12] by full-matrix least-squares methods. Absorption corrections were made for every structure. Hydrogen atoms were introduced at calculated positions

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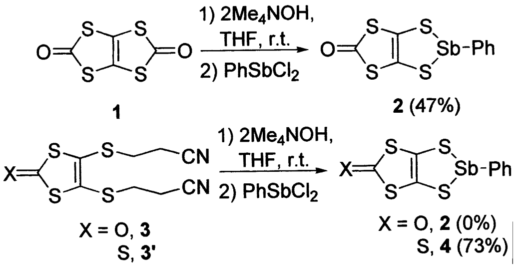
Table 1. Crystallographic Data

	2	5	8a	8b	9	10
formula	$C_9H_5OS_4Sb$	$C_{20}H_{29}N_2O_2S_8Sb$	$C_{26}H_{30}NO_2S_8Sb$	$C_{26}H_{30}NO_2S_8Sb$	$C_{26}H_{30}NS_{10}Sb$	$C_{26}H_{30}NOS_9Sb$
fw	379.12	707.68	766.74	766.74	798.86	782.80
temp (K)	293	250	293	293	293	293
cryst syst	monoclinic	orthorhombic	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_12_12_1$ (No. 19)	$P2_1/c$ (No. 14)	$Pbca$ (No. 61)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	10.087(2)	12.606(3)	16.1301(10)	18.886(4)	16.800(3)	16.503(3)
b (Å)	16.123(3)	14.742(3)	12.5159(10)	12.885(3)	12.457(3)	12.462(3)
c (Å)	14.689(3)	16.379(3)	17.0510(10)	26.254(5)	17.418(4)	17.325(4)
β (deg)	99.06(3)	90.00	112.161(10)	90.00	112.94(3)	112.92(3)
V (Å^3)	2359.1(8)	3044.0(10)	3188.0(4)	6389(2)	3356.6(12)	3281.8(11)
Z	8	4	4	8	4	4
d_{calcd} (g cm^{-3})	2.135	1.544	1.597	1.594	1.581	1.584
μ (mm^{-1})	3.014	1.475	1.415	1.412	1.463	1.436
λ(Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
cryst size (mm)	0.25 × 0.08 × 0.03	0.25 × 0.25 × 0.2	0.52 × 0.3 × 0.1	0.3 × 0.2 × 0.13	0.7 × 0.32 × 0.1	0.66 × 0.1 × 0.08
2θ range (deg)	3.8−51.7	4.1−52.1	2.8−52.0	3.8−51.8	4.1−51.9	4.1−51.8
no. of unique rflns	4433	5915	6243	6114	6408	6281
no. of obsd data ($I > 2\sigma(I)$)	3593	4659	4651	3816	4636	4097
no. of params	271	306	343	343	343	361
R1	0.026	0.031	0.032	0.032	0.025	0.029
wR2 (all data)	0.053	0.056	0.095	0.057	0.045	0.054
goodness of fit	0.98	0.98	1.10	0.86	0.85	0.82

Scheme 1



(riding model), included in structure factor calculations, and not refined. All the heavy atoms were refined anisotropically.

Results and Discussion

Synthesis and Crystal Structure of PhSb(dmid). The first attempts to synthesize the complex **2** consisted of deprotection of 4,5-bis((2-cyanoethyl)thio)-1,3-dithiole-2-one (**3**) with 2 equiv of base, followed by reaction with phenyldichlorostibine, but for any deprotection conditions we tried, such as different bases and solvents, no desired compound was recovered. This preference for the starting reagent **3** was motivated by the successful synthesis of PhSb(dmit) (**4**) by the same route, using **3′** as the protected dmit and Me_4NOH as base (Scheme 1).

This preparation method of **4** parallels that already published,[6] although a higher yield has been now obtained. The failure of this method in the synthesis of **2** is very likely due to the competition between hydrogen abstraction in the position α to the CN group and nucleophilic attack on C═O, leading to a mixture of thiolates. Reaction of compound **1**, the masked dmid, by deprotection with base and quenching with $PhSbCl_2$ afforded **2** as a yellow solid. A fast addition of dichlorophenylstibine in the dithiolate solution appears to be crucial; otherwise, **2** is obtained in very low yield, as discussed below. Assignment of ^{1}H and ^{13}C NMR signals were made by comparison with published data for PhSb(dmit)[6] and R_2Sn(dmid)[13] complexes. PhSb(dmid) crystallizes in the monoclinic system, space group $P2_1/c$, with two independent molecules, named as Sb1 and Sb2 hereafter, on general positions in the unit cell, which are not chemically significantly different (Figure 1).

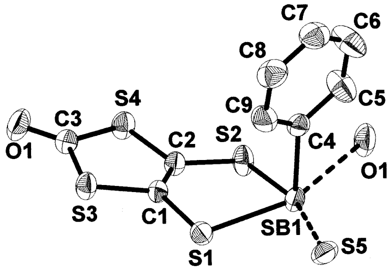


Figure 1. ORTEP view and numbering scheme of one independent molecule (Sb1) of PhSb(dmid), with 50% probability displacement ellipsoids. Hydrogen atoms have been omitted. Dashed bonds represent intermolecular short contacts.

The primary coordination pattern about Sb atom consists, as expected, of two S (dithiolato) atoms and one C (ipso) atom, with the phenyl group practically perpendicular to the S−Sb−S plane, and values for bond lengths and angles in the normal range (Table 2).

In both independent molecules, the antimony atom completes its coordination sphere by two secondary contacts of Sb- - -O and Sb- - -S type, shorter than the sum of van der Waals radii (about 3.6 and 3.9 Å, respectively),[14] located in the least-squares equatorial plane along with the two dithiolene sulfur atoms. The deviation of Sb from this mean plane amounts to 0.1 Å for Sb1 and 0.36 Å for Sb2. The Sb- - -O contacts, with values of 2.891(3) Å for Sb1 and 3.422(3) Å for Sb2, are established between the same type of molecules, whereas a crossed situation is observed for the Sb- - -S (thiolato) interactions, with values of 3.422(1) Å (Sb1- - -S5) and 3.315(1) Å (Sb2- - -S1). Altogether, the coordination geometry around Sb is of distorted-octahedral type if one takes into account the 5s^2 lone pair, probably lying trans to the phenyl group. An interesting geometrical parameter, characteristic for a coordinated dithiolene

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[13] Chohan, Z. H.; Howie, R. A.; Wardell, J. L. *J. Organomet. Chem.* **1999**, *577*, 140.

[14] (a) Bondi, A. J. *J. Phys. Chem.* **1964**, *68*, 441. (b) Spackman, M. A. *J. Chem. Phys.* **1986**, *85*, 6579.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 2 and 5

Compound 2			
Bond Lengths			
Sb1−S1	2.493(1)	Sb2−S5	2.497(1)
Sb1−S2	2.466(1)	Sb2−S6	2.449(1)
Sb1−C4	2.163(3)	Sb2−C13	2.139(4)
Sb1- - -O1	2.891(3)	Sb2- - -O2	3.422(3)
Sb1- - -S5	3.422(1)	Sb2- - -S1	3.315(1)
Bond Angles			
S1−Sb1−S2	86.68(3)	S5−Sb2−S6	85.95(4)
S1−Sb1−C4	95.71(9)	S5−Sb2−C13	100.48(9)
S2−Sb1−C4	100.35(9)	S6−Sb2−C13	97.30(10)
S1−Sb1−S5	76.27(3)	S6−Sb2−S1	74.23(3)
S2−Sb1−O1	65.31(6)	S5−Sb2−O2	72.12(7)
S5−Sb1−O1	131.44(5)	S1−Sb2−O2	125.51(7)
Compound 5			
Bond Lengths			
Sb1−S1	2.935(1)	Sb1−S6	2.569(1)
Sb1−S2	2.576(1)	Sb1−C7	2.171(4)
Sb1−S5	2.871(1)		
Bond Angles			
S1−Sb1−S2	78.89(4)	C7−Sb1−S1	86.78(12)
S5−Sb1−S6	77.18(5)	C7−Sb1−S2	91.88(13)
S1−Sb1−S5	118.14(4)	C7−Sb1−S5	83.48(12)
S2−Sb1−S6	85.89(4)	C7−Sb1−S6	95.50(13)

ligand, is the dihedral angle about the S- - -S hinge within the five-membered C_2S_2Sb metallacycle. We can observe from Table 4 that the values for Sb1 and Sb2 are quite different, although the distortion is in the same direction. Theoretical calculations in the case of heteroleptic dithiolene complexes have shown that the rotation barrier around the S- - -S axis is rather low: hence, the role of packing forces in this type of distortion.[15] The alternate Sb1- - -S5 and Sb2- - -S1 short secondary contacts run in such a manner that they lead to the formation of a centrosymmetric cyclic octagonal "Sb_4S_4" motif, represented in Figure 2, as a result of a formal tetramerization of the PhSb(dmid) molecule.

This type of cyclic pattern can be also identified in the structure of open-framework antimony sulfides.[5b] The octagon is "compressed" along the Sb2- - -Sb2 axis, the corresponding distance, which amounts to 3.963(1) Å, being shorter by about 0.3 Å than the sum of van der Waals radii of two Sb atoms.[16] Furthermore, each $[Ph(Sb(dmid)]_4$ tetramer is not isolated but interacts with eight other tetramers via Sb- - -O interactions, thus leading to the formation of an original extended 3D network. Unlike the structure of PhSb(dmit), of chain-like type with transversal S- - -S interactions, no short intermolecular S- - -S contacts occur this time. In conclusion, counting on the the coordinative unsaturation of the Sb(III) center, we induced a huge modification of the 3D network in the crystalline state when comparing the structures of PhSb(dmit) and PhSb(dmid), only by changing C=S with C=O in the structure of the dithiolene ligand.

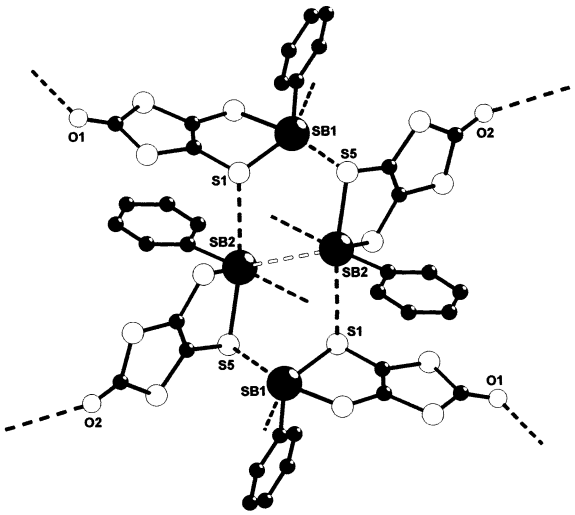
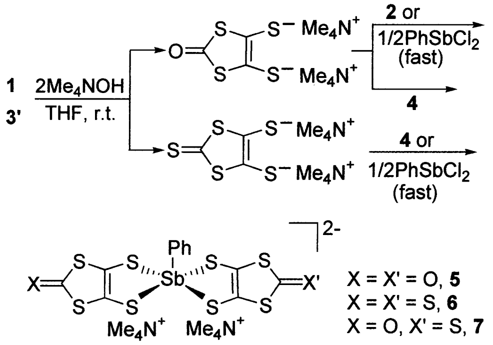


Figure 2. "Sb_4S_4" tetrameric motif in the structure of PhSb(dmid). Dashed, filled bonds represent intermolecular Sb- - -S or Sb- - -O contacts, whereas the dashed, open bond evidences the intermolecular Sb2- - -Sb2 contact.

Scheme 2



Synthesis and Characterization of $[PhSb^{III}(dithiolene)_2]^{2-}$ Complexes. As mentioned earlier, a slow addition of $PhSbCl_2$ in the dithiolate suspension leads to a low yield in PhSb(dmid) but afforded instead the salt of the $[Ph_2Sb(dmid)_2]^-$ anion, with Sb in the +5 oxidation state coordinated to two dithiolene ligands (vide infra). This Sb(V) species is likely to be formed by oxidation of a dianionic $[PhSb^{III}(dmid)_2]^{2-}$ intermediate. The latter was indeed obtained from the reaction of 1 equiv of neutral PhSb(dmid) with $(Me_4N)_2$(dmid) or by the fast addition of 0.5 equiv of $PhSbCl_2$ in a $(Me_4N)_2$(dmid) suspension (Scheme 2). **5** was purified by recrystallization in CH_3CN to afford an orange crystalline solid sensitive to oxygen and moisture.

The complex crystallized in the orthorhombic system, space group $P2_12_12_1$, with the two Me_4N^+ cations and the dianion (Figure 3) in general positions in the unit cell. Values for bond lengths and angles are listed in Table 2.

Interestingly, both dithiolene ligands are coordinated in an unsymmetrical manner on the antimony center, with one "short" and one "long" antimony−sulfur bond for each of them. The "short" bonds, Sb1−S2 (2.576(1) Å) and Sb1−S6 (2.569(1) Å), are on average about 0.1 Å longer than Sb−S bonds in neutral complexes, whereas the "long" bonds, Sb1−S1 (2.935(1) Å) and Sb1−S5 (2.871(1) Å), are significantly longer and approach the characteristic values for secondary Sb- - -S contacts.[5] This latter feature suggests that S1 and S5 bear an important negative charge and, hence, a significant

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(15) Domercq, B.; Coulon, C.; Fourmigué, M. *Inorg. Chem.* **2001**, *40*, 371.

(16) Much shorter intermolecular Sb- - -Sb contacts, of about 3.6−3.7 Å, have been observed in the solid-state structure of distibines presenting a thermochromic activity: (a) Ashe, A. J., III; Butler, W.; Diephouse, T. R. *J. Am. Chem. Soc.* **1981**, *103*, 207. (b) Mundt, O.; Riffel, H.; Becker, G.; Simon, A. *Z. Naturforsch., B* **1984**, *39B*, 317.

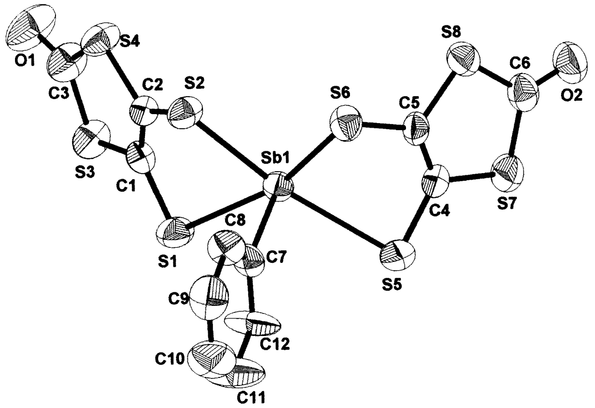


Figure 3. ORTEP view and numbering scheme of $[PhSb(dmid)_2]^{2-}$ in **5**, with 50% probability displacement ellipsoids. Hydrogen atoms have been omitted.

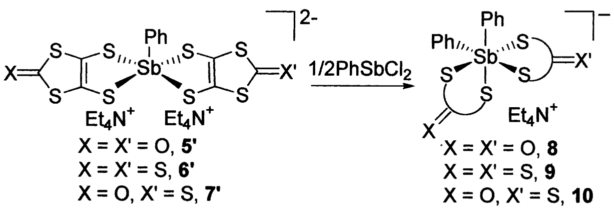
nucleophilic character, which could explain the further reactivity of the complex. The four coordinating sulfur atoms are in the equatorial plane, with a relative cis arrangement of the "short" and, respectively, "long" Sb−S bonds, from which Sb deviates by about 0.06 Å. The phenyl ring is practically perpendicular to this plane, and the Sb lone pair is very likely located trans to C_{ipso}, which leads to a distorted-octahedral coordination geometry. Since the antimony is pentacoordinated, this geometry should be fluxional in solution.[17] Both dithiolene ligands are highly folded (38.87 and 54.81°, respectively) along the S- - -S hinge, with distortions in the opposite direction when compared with the neutral PhSb(dmid) (Table 4). No additional intermolecular Sb- - -S or S- - -S short contacts are observed within this structure, which represents the first example of a dianionic antimony dithiolene complex.

The same strategy was applied to the synthesis of **6**, the dmit analogue of **5**, by deprotection of **3** with $Me_4N^+OH^-$, followed by the reaction of the resulting dithiolate with 1 equiv of PhSb(dmit). The mixed dmid/dmit dianion **7** was also synthesized, by base deprotection of the dmid precursor **1** and trapping with 1 equiv of PhSb(dmit). Very likely, this mixed bis(dithiolene) complex is a statistical mixture of **5**−**7**, with eventually a preference for the unsymmetrical compound as observed in mixed nickel bis(dithiolene) complexes.[18] By the successful preparation of this series of dianionic complexes **5**−**7**, we have in our hands the supposed key intermediates in the synthesis of the $[Ph_2Sb^V(dithiolene)_2]^-$ type complexes.

Synthesis and Characterization of $[Ph_2Sb^V(dithiolene)_2]^-$ Complexes. Mechanistic Discussions. To study the reactivity of the $[PhSb^{III}(dithiolene)_2]^{2-}$ series with a second 1 equiv of $PhSbCl_2$, the dianions **5′**−**7′** have been generated as NEt_4^+ salts, since they are more soluble than the corresponding NMe_4^+ salts **5**−**7**. Addition of $PhSbCl_2$ to the suspension of **5′** and purification workup afforded the complex **8** as the single reaction product, in a moderate yield (Scheme 3).

Attempts to isolate or to identify other reaction byproducts have been unsuccessful. The structure of **8** was established by a single-crystal X-ray measurement. Single crystals of the first polymorph, named **8a**, have been grown by slow diffusion of hexane into a THF solution of the complex. The compound crystallized in the monoclinic system, space group $P2_1/c$, with one anion and one tetrahedral ammonium cation in general positions. An ORTEP representation of $[Ph_2Sb(dmid)_2]^-$ is shown in Figure 4, and important bond lengths and angles are listed in Table 3.

Scheme 3



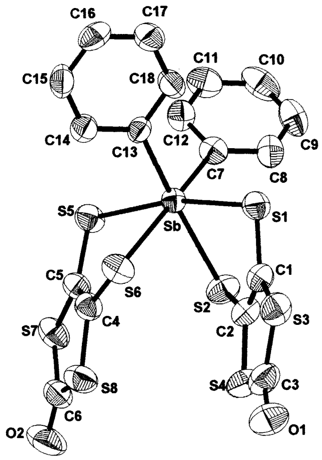


Figure 4. ORTEP view and numbering scheme of $[Ph_2Sb(dmid)_2]^-$ in **8a**, with 50% probability displacement ellipsoids. Hydrogen atoms have been omitted.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 8a and 8b

	8a	8b
	Bond Lengths	
Sb−S1	2.540(1)	2.557(1)
Sb−S2	2.628(1)	2.608(1)
Sb−S5	2.534(1)	2.529(1)
Sb−S6	2.640(1)	2.577(1)
Sb−C7	2.170(5)	2.165(3)
Sb−C13	2.158(5)	2.153(3)
	Bond Angles	
S1−Sb−S2	80.11(5)	79.25(4)
S5−Sb−S6	80.33(5)	80.55(4)
S1−Sb−S6	89.69(5)	92.36(4)
S2−Sb−S5	90.69(5)	94.70(3)
S2−Sb−S6	86.30(5)	80.71(3)
C7−Sb−S1	96.83(14)	91.55(9)
C7−Sb−S2	89.74(14)	89.52(9)
C7−Sb−S5	92.42(14)	94.54(9)
C7−Sb−C13	94.18(19)	98.00(12)
C13−Sb−S1	92.46(13)	92.46(10)
C13−Sb−S5	96.14(13)	92.72(10)
C13−Sb−S6	90.67(14)	92.52(10)

The antimony center, now in the +5 oxidation state, is hexacoordinated, within a distorted-octahedral field. In such an environment, Sb(V) is coordinatively saturated: hence, the absence of any Sb- - -S or Sb- - -O secondary short contact. One can note the cis arrangement of the phenyl groups; therefore, each dithiolene

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[17] Barucki, H.; Coles, S. J.; Costello, J. F.; Hursthouse, M. B. *J. Organomet. Chem.* **2001**, *622*, 265.

[18] (a) Davison, A.; McCleverty, J. A.; Shawl, E. T.; Wharton, E. J. *J. Am. Chem. Soc.* **1967**, *89*, 830. (b) Kato, R.; Kashimura, Y.; Sawa, H.; Okano, Y. *Chem. Lett.* **1997**, 921.

Table 4. Dihedral Angles[a] (deg)

	S1−Sb−S2	S5−Sb−S6
2	−19.71(7)	−26.17(11)
5	38.87(16)	54.81(10)
8a	43.08(21)	39.64(12)
8b	−49.68(10)	−49.51(10)

[a] Negative values correspond to a dithiolene deviation toward the phenyl rings.

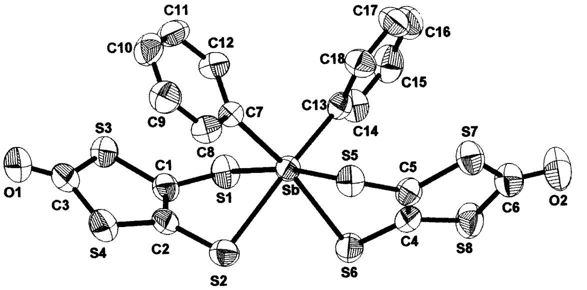


Figure 5. ORTEP view and numbering scheme of $[Ph_2Sb(dmid)_2]^-$ in **8b**, with 50% probability displacement ellipsoids. Hydrogen atoms have been omitted.

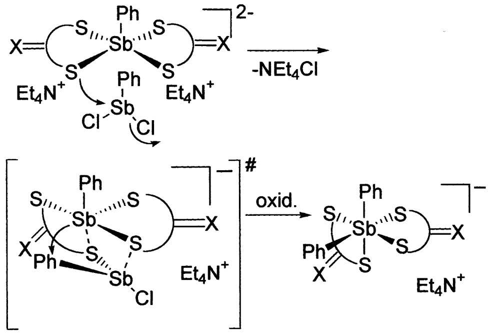
ligand is unsymmetric, with distances slightly longer for the Sb−S bonds trans to Sb−C_{ipso} than for the pair of Sb−S bonds trans to each other. Nevertheless, bond lengths and angles are in the usual range.[11,19] Both dithiolene ligands are highly folded along the S- - -S hinge, back toward the phenyl rings, in a face-to face conformation, with calculated values for the dihedral angles of 43.08° (S1- - -S2) and 39.64° (S5- - -S6) (Table 4).

Interestingly, the dithiolene folding is in the opposite direction, toward the phenyl rings, in the case of the second polymorph **8b**, represented in Figure 5, crystallized this time by cooling a THF−toluene solution of **8**. The two dihedral angles have now values of −49.68° (S1- - -S2) and −49.51° (S5- - -S6). This second polymorph crystallized in the orthorhombic system, space group *Pbca*, with the anion and cation in general positions.

Bond lengths and angles (Table 3) are in the normal range, the only striking difference on comparison with **8a** being the torsion angles previously discussed. At room temperature the molecule is fluxional in solution on the NMR time scale. Indeed, the phenyl groups are equivalent by ^1H and ^{13}C NMR, as well as the dithiolene ligands by ^{13}C NMR. Furthermore, in ^{13}C NMR spectra we can observe two signals for the C═C dithiolene carbon atoms, at 121.5 and 128.1 ppm, proving that we have only the cis stereoisomer in solution, since the two carbon atoms in each dithiolene are connected to nonequivalent sulfur atoms.

Formation of $[Ph_2Sb^V(dithiolene)_2]^-$ complexes directly from dithiolates and $PhSbCl_2$ represents an original and elegant route to synthesize the former class of compounds. The mechanism of this unprecedented transformation in antimony series very likely involves, in a first step, the generation of reactive $[PhSb^{III}(dithiolene)_2]^{2-}$ dianions. Isolation and unambiguous characterization of these latter compounds (vide supra) strongly support our first mechanistic hypothesis. Subsequently, the reaction of intermediary dianions with a second 1 equiv of $PhSbCl_2$ appears to be more complex, since it implies the phenyl transfer accompanied by the oxidation of Sb(III) in Sb(V). However, we can attempt to explain this second stage (Scheme 4) and reasonably imagine a nucleophilic attack of a coordinated sulfur atom, still bearing an important negative charge (vide supra), on $PhSbCl_2$ leading to an intermediate adduct with concomitant elimination of 1 equiv of NEt_4Cl.

Scheme 4



In the adduct, the antimony atoms would be bridged by two sulfur atoms, thus forming a "Sb_2S_2" motif, and in such a conformation a secondary Sb- - -Ph contact could be established, previous to the effective phenyl transfer. This kind of weak Sb- - -Ph interaction occurs in solid-state structures of $Ar{\cdot}SbX_3$ (X = Cl, Br) compounds,[20] also known as *Menshutkin* type complexes,[21] or of $[PPh_4]_2[Sb_2X_8]$ (X = Br, I) salts.[22] Then a phenyl transfer would lead to the final $[Ph_2Sb^V(dithiolene)_2]^-$ after oxidation. Unfortunately, we could not isolate or identify any but $[Ph_2Sb(dithiolene)_2]^-$−antimony-containing compounds in the resulting reaction mixture.

By applying method A to the appropriate dmit precursor **3′**, we synthesized the $[Ph_2Sb(dmit)_2]^-$ salt **9**, the sulfur counterpart of **8** (Scheme 3). Preparation of complex **9** by a different route, involving the reaction of preformed Sb(V) Ph_2SbCl_3 with $[NEt_4]_2[Zn(dmit)_2]$ in the presence of KSCN, was previously reported by Wardell et al.[11] The authors described, along with IR and ^1H NMR data, the X-ray structure of the compound, which was solved in the monoclinic system, space group $P2_1/n$. In our case, **9** crystallized in the monoclinic system, space group $P2_1/c$. One can observe that this complex is isostructural with **8a**; therefore, no further structural parameters will be discussed here but, rather, in the Supporting Information. The distortion of dmit ligands, in a face-to-face conformation and with corresponding dihedral angles amounting to about 40°, is exactly the same as in **8a**. In the ^{13}C NMR spectrum two signals, at 135.1 and 141.7 ppm, are observed for C═C carbon atoms. This feature, along with the singlets observed for C_{ipso} and C═S carbon atoms, unambiguously indicates the cis stereochemistry of **9** also in solution.

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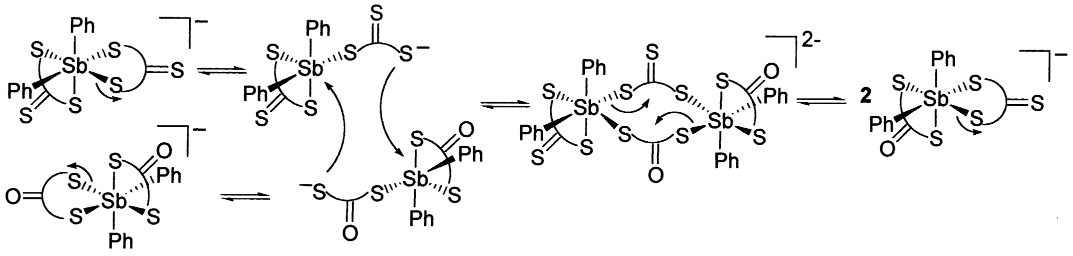
(19) Spencer, G. M.; Wardell, J. L.; Aupers, J. H. *Polyhedron* **1996**, *15*, 2701.

(20) (a) Mundt, O.; Becker, G.; Stadelmann, H.; Thurn, H. *Z. Anorg. Allg. Chem.* **1992**, *617*, 59. (b) Schmidbaur, H.; Nowak, R.; Huber, B.; Müller, G. *Organometallics* **1987**, *6*, 2266. (c) Hulme, R.; Mullen, D. J. E. *J. Chem. Soc., Dalton Trans.* **1976**, 802.

(21) Menshutkin, B. N. *Zh. Russ. Fiz. Chim. Ova.* **1911**, *43*, 1298.

(22) (a) Pohl, S.; Saak, W.; Haase, D. *Angew. Chem.* **1987**, *99*, 462. (b) Pohl, S.; Saak, W.; Lotz, R.; Haase, D. *Z. Naturforsch., B* **1990**, *45B*, 1355.

Scheme 5



The mixed dmid/dmit Sb(V) dithiolene complex, $[NEt_4][Ph_2Sb^V(dmit)(dmid)]$ (**10**), was also synthesized by generating first the mixed dianion $[NEt_4]_2[PhSb^{III}(dmit)(dmid)]$ (**7′**), which was then quenched by 1 equiv of $PhSbCl_2$, as depicted in Scheme 3. Single crystals of **10**, grown by slow diffusion of hexane into a THF solution of the complex, crystallized in the monoclinic system, group space $P2_1/c$, and the compound proved to be isostructural with its congeners **8a** and **9**. An occupational disorder was found for terminal C═X (X = O, S) and refined at 0.6 O and 0.4 S5′ occupational factors for C6═X and 0.4 O′ and 0.6 S5 occupational factor for C3═X. However, this X-ray measurement did not allow us to determine whether we crystallized a pure compound or cocrystallized a statistic mixture of **8a**, **9**, and **10**. ^{13}C NMR spectra of THF-d_8 solutions of **10**, one obtained from single crystals and the other from a powder, were similar, with signals characterizing a mixture of **8**−**10** in a roughly statistical (1/1/2) ratio. The question arises whether this statistical mixture is only the consequence of the obvious rearrangement, previous to the reaction with $PhSbCl_2$, of the intermediary dianion **7**, in fact a mixture of **5**−**7**, or if also **8**−**10**, once formed, are in equilibrium in solution. The ^1H and ^{13}C NMR spectra of a solution of mixture of **8**−**10** obtained by the "normal" synthetic procedure and those of a solution obtained from equimolar amounts of **8** and **9** and measured immediately after mixing are exactly the same, demonstrating the formation of the mixed $[Ph_2Sb(dmit)(dmid)]^-$ salt from **8** and **9** and showing that the coordination of dithiolene ligands on the Sb(V) center is quite labile, even in an octahedral environment. A plausible redistribution mechanism (Scheme 5) would involve a partial decoordination of a dithiolene to a five-coordinate antimony species followed by a concerted fast ligand exchange between two such intermediates. Otherwise, a complete decoordination of a dithiolene seems quite unlikely. The question whether there is also a phenyl scrambling within these Sb(V) complexes still remains open.

All these experimental results show that the currently studied organoantimony dithiolene complexes are highly fluxional in solution and sensitive to the presence of other donor or acceptor groups, which express the flexibility of the antimony coordination sphere on one hand and that of the coordinated dithiolene on the other hand. Interestingly, the former aspect was nicely explored in solution in catalytic processes, as for example the polycondensation of bis(hydroxyethyl)terephthalate (BHET), in which antimony(III)-containing complexes, such as antimony ethylene glycolate $[Sb_2(OCH_2CH_2O)_3]_n$, were utilized as catalysts.[23] Conversely, both features can lead in the solid state to a huge variety of structures, as emphasized through the examples described so far.

Conclusions

New neutral and anionic organoantimony dithiolene complexes have been synthesized and characterized. The neutral complex PhSb(dmid) forms an original 3D network in the solid state, based on interacting octagonal cyclic motifs of "Sb_4S_4" type. Short intermolecular Sb- - -S and Sb- - -O contacts have been identified in this structure. To rationalize the unexpected formation of the anionic $[Ph_2Sb^V(dmid)_2]^-$ complex as a secondary product in the synthesis of PhSb(dmid), we prepared a series of highly reactive $[PhSb^{III}(dithiolene)_2]^{2-}$ salts. These were thought to be key intermediates in the new and original synthesis of $[Ph_2Sb^V(dithiolene)_2]^-$ complexes. By analyzing the single-crystal X-ray structure of $[Me_4N]_2[PhSb^{III}(dmid)_2]$, in which Sb(III) center is coordinated in a distorted octahedral field if we consider the lone pair, we can conclude that two out of four coordinated sulfur atoms bear an important negative charge. This explains the reactivity of $[PhSb^{III}(dithiolene)_2]^{2-}$ toward $PhSbCl_2$ leading to the series of $[Ph_2Sb^V(dithiolene)_2]^-$ species. These latter species are octahedral complexes, as determined by single-crystal X-ray measurements, and in the case of $[Ph_2Sb(dmid)_2]^-$ two polymorphs, differing in the coordinated dithiolene conformation, have been crystallized. The fluxionality of these complexes in solution, expressed in a fast dithiolene exchange, has been evidenced by NMR measurements.

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Supporting Information Available: Crystallographic data, bond distances, bond angles, anisotropic displacement parameters, and all atom coordinates and thermal parameters in CIF format and figures giving NMR spectra for compounds **5**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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