Electron-Rich Organoantimony(III) Dithiolate Complexes

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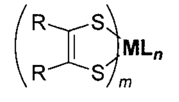
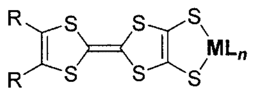
Keywords: Antimony / Noncovalent interactions / S ligands / X-ray diffraction

Electron-rich dithiolene complexes of the antimony(III) PhSb moiety, formulated as [SbPh(dddt)] (**1**) (dddt: 5,6-dihydro-1,4-dithiine-2,3-dithiolate) and [SbPh(EDT-TTFS$_2$)] (**2**) (EDT-TTFS$_2$: 4,5-ethylenedithio-tetrathiafulvalene-4′,5′-dithiolate), have been prepared by deprotection of the corresponding precursors and trapping of the intermediate dithiolates with PhSbCl$_2$. Both complexes have been structurally characterized. The analysis of their single-crystal X-ray structures shows original supramolecular organizations governed by secondary Sb···S contacts, with distorted octahedral coordination geometries around the Sb center. Band-structure calculations for complex **2** reveal only weak dispersion of the valence and conduction bands, with an energy gap of 1.68 eV.

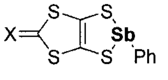
Introduction

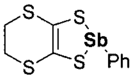
Following their discovery in the 1960s,[1] homoleptic dithiolene complexes,[2] and particularly the square-planar complexes of d^8 metal cations (Ni, Pt, Pd), became the subject of extensive investigations,[3] mainly oriented toward the preparation and understanding of their magnetic[4] and conducting (eventually superconducting) salts.[5] In that respect, heteroleptic complexes, which involve one or more dithiolate ligands together with other ligands (bipy, dppe, Cp, CN,....) in the metal coordination sphere, have been much less investigated,[6,7] despite a wide variety of possible applications, for example as luminescent[8] or magnetic systems.[9] More recently, the dithiolate ligand built directly on a tetrathiafulvalene core (TTFS$_2^{2-}$) (TTFS$_2^{2-}$: tetrathiafulvalene-4,5-dithiolate) became available[10,11] and prompted the preparation of a wealth of novel dithiolene complexes, such as the homoleptic ones — the square-planar metallic Ni, Pt or Pd complexes described by Kobayashi and co-workers[12,13] or the tris(dithiolene) vanadium complexes[14] — or heteroleptic ones of general formula [ML$_n$(TTFS$_2$)] [ML$_n$ = TiCp$_2$,[15] Ni(CN)$_2$,[16] Pt(bipy),[17,18] CoCp,[19] Pt(dppe),[20] Au(py-Ph),[21] M(dppf),[22]...]. These tetrathiafulvalene-4,5-dithiolate complexes are particularly attractive since they combine the properties of the TTF core with those of the dithiolene complex moiety.

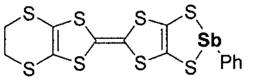

(dt)$_m$ML$_n$ complexes


(TTFS$_2$)ML$_n$ complexes

We recently became interested in main-group derivatives of such heteroleptic dithiolene complexes and concentrated on the antimony moiety SbPh as the ML$_n$ group in order to take advantage of both the diffuse lone pair of the Sb^{III} and its capacity to exhibit secondary coordination.[23] Indeed, in [SbPh(dmit)]·(THF) (dmit: 1,3-dithiole-2-thione-4,5-dithiolate),[24] the oxygen atom of the THF molecule and the outer sulfur atom of the C=S fragment enter the antimony coordination sphere of neighboring molecules, affording dimerized infinite chains stabilized by these Sb···O and Sb···S interactions. The flexibility of the coordination around antimony is further demonstrated by the observation of two successive single-crystal structural phase-transitions. On the other hand, in [SbPh(dmid)],[25] secondary Sb···S contacts lead to the formation of a centrosymmetric cyclic octagonal "Sb$_4$S$_4$" motif as a result of a formal tetramerization of the [SbPh(dmid)] molecule. Such motifs are also encountered in open-framework antimony sulfides.[26]


X = S PhSb(dmit)
X = O PhSb(dmid)


PhSb(dddt)


(EDT-TTFS$_2$)SbPh

Although [SbPh(dmit)] and [SbPh(dmid)] differ only in the terminal chalcogen C=X (X = O, S) atom, they have rather distinct structures, demonstrating a very high structural flexibility in the solid state thanks to secondary Sb···S and Sb···O contacts in which the terminal chalcogen is always involved. This prompted us to investigate Sb^{III}-based dithiolene complexes with a completely different backbone

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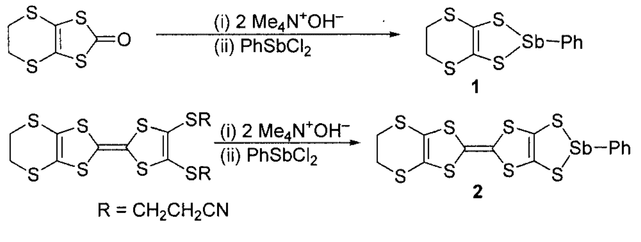
DOI: 10.1002/ejic.200400192

in order to study the structural adaptability of the system, and we focused on more electron-rich dithiolate ligands, thus keeping an eye on the possibility of accessing open-shell species upon oxidation. Therefore, complexes derived from dddt^{2-} and EDT-TTFS$_2{}^{2-}$ have been prepared. Their solid-state crystalline structures along with the band-structure calculation for the TTF-based compound are reported here.

Results and Discussion

Syntheses

Deprotection of 5,6-dihydro-[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-one[27] with two equivalents of (Me$_4$N·OH) in THF leads to the formation of the corresponding dithiolate dddt^{2-}. Subsequent fast addition of PhSbCl$_2$,[28] followed by purification workup, afforded **1** as an orange solid (Scheme 1). The elemental analysis and ^{1}H NMR spectroscopic data are in agreement with the proposed formulation. Suitable single crystals for an X-ray analysis (vide infra) were grown by slow evaporation of the solvent from a CH$_2$Cl$_2$ solution of the complex. Similarly, deprotection of 4,5-bis[(2-cyanoethyl)thio]-4′,5′-ethylenedithiotetrathiafulvalene[29,30] with two equivalents of (Me$_4$N·OH) in THF afforded the highly air sensitive TTF dithiolate. This was quenched with PhSbCl$_2$ to give complex **2**, which was analyzed by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis. Red crystals of **2**, suitable for an X-ray analysis, were obtained by recrystallization from toluene. The complex is readily soluble in THF and only sparingly soluble in other organic solvents. As described in our previous study,[25] the addition rate of PhSbCl$_2$ is a crucial parameter in order to reach an optimum yield of the dithiolene complex. This is related to the reactivity of **1** or **2**, once formed, towards a second equivalent of dithiolate to give a highly reactive dianionic species. A fast addition of PhSbCl$_2$ to the dithiolate suspension ensures a good yield of the desired product.



Scheme 1

Structure of [SbPh(dddt)]

The complex crystallizes in the triclinic system, space group $P\bar{1}$, with three crystallographically independent molecules (noted A, B and C in the following) in the unit cell, together with one CH$_2$Cl$_2$ molecule (Figure 1). Selected intramolecular bond lengths and bond angles for each of the molecules are listed in Table 1 and 2, respectively. They are similar to those observed in [SbPh(dmit)] and [SbPh(dmid)], with a primary coordination pattern around the antimony atom consisting, as expected, of two S (dithiolate) atoms and one C(*ipso*) atom, with the phenyl group almost perpendicular to the S−Sb−S plane. The folding angle of the SbS$_2$C$_2$ metallacycle along the S···S hinge, a characteristic of coordinated dithiolene complexes, amounts to 31.89(23)°, 24.23(27)° and 26.98(18)° in molecules A−C, respectively. The differences between the three molecules are not so important if one takes into account that the rotation barrier of such metallacycles is rather low.[9] Every molecule completes its coordination sphere by a complex set of secondary Sb···S interactions (Figure 2). Both Sb1A and Sb1B exhibit two short Sb···S contacts with sulfur atoms of neighboring molecules located in the least-square equatorial plane along with the two dithiolene sulfur atoms (see Table 1). The intermolecular Sb···S distances lie between 3.31 and 3.61 Å, well below the sum of the van der Waals radii (3.80 Å).[31] Altogether, the coordination around Sb1A and Sb1B is of distorted octahedral type if one takes into account the 5s^2 lone pair, probably lying *trans* to the phenyl group. On the other hand, Sb1C engages in only one such Sb···S secondary interaction and appears, from that point of view, coordinatively unsaturated. These secondary interactions around Sb1A and Sb1B give rise to the formation of an eight-membered ring with alternating Sb and S atoms. The resulting tetramolecular Sb$_4$S$_4$ units

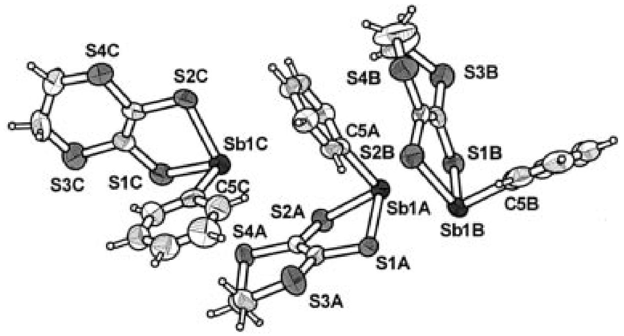


Figure 1. ORTEP drawing of the three crystallographically independent PhSb(dddt) molecules along with their numbering scheme

Table 1. Selected bond lengths (Å) for [SbPh(dddt)]; symmetry transformations used to generate equivalent atoms: (a) *x*, *y*, *z*; (b) 1 − *x*, −*y*, 1 − *z*; (c) 2 − *x*, −*y*, 1 − *z*; (d) 1 + *x*, *y*, *z*

Molecule A			
Sb1A−S1A	2.458(2)	Sb1A−C5A	2.149(8)
Sb1A−S2A	2.475(2)		
Sb1A···S1B^a	3.31(2)	Sb1A···S1C^b	3.42(2)
Molecule B			
Sb1B−S2B	2.451(3)	Sb1B−C5B	2.133(9)
Sb1B−S1B	2.468(2)		
Sb1B···S2A^c	3.43(4)	Sb1B···S2C^d	3.61(2)
Molecule C			
Sb1C−S1C	2.435(3)	Sb1C−C5C	2.156(8)
Sb1C−S2C	2.463(3)		
Sb1C···S4A^a	3.36(5)		

are connected together by two molecules C, affording infinite chains running along the *a*-axis. These chains are well separated from each other by: (i) the phenyl and ethylene groups of the constituting molecules, which point toward the outside of the columns, and (ii) by disordered CH_2Cl_2 molecules included into the channels formed between the columns. These Sb_4S_4 cyclic patterns have also been identified in the structure of [SbPh(dmid)], while Sb_2S_2 motifs are found in [SbPh(dmit)]. They are also frequently observed in the open-framework antimony sulfides based on the primary Sb−S bonds.

Table 2. Selected bond angles (°) for [SbPh(dddt)] (**1**)

Molecule A			
C5A−Sb1A−S1A	95.9(2)	S1A−Sb1A−S2A	84.40(7)
C5A−Sb1A−S2A	93.2(2)		
Molecule B			
C5B−Sb1B−S2B	94.1(2)	S2B−Sb1B−S1B	85.30(8)
C5B−Sb1B−S1B	96.0(2)		
Molecule C			
C5C−Sb1C−S1C	94.9(3)	S1C−Sb1C−S2C	85.04(8)
C5C−Sb1C−S2C	95.0(2)		

Structure of [SbPh(EDT-TTFS$_2$)]

The complex crystallizes in the orthorhombic system, space group $Pca2_1$ with one molecule in a general position in the unit cell (Figure 3). Intramolecular bond lengths and angles are in the usual range (Table 3). The EDT-TTF moieties stack on top of each other along the *b*-axis. As often observed with neutral tetrathiafulvalene derivatives, the dithiole rings are folded along the S···S hinge, by 19.97(69)° on the ethylenedithio side and by 13.30(63)° on the metallacycle side. On the other hand, the metallacycle itself is also distorted, with a folding along the S···S hinge of 19.09(32)°, weaker than that observed in [SbPh(dddt)]. The antimony coordination sphere (Figure 4) is completed by four Sb···S secondary interactions, two of them with sulfur atoms (S7, S8) located in the least-square equatorial plane along with the two dithiolene sulfur atoms (Sb···S7: 3.85 Å; Sb···S8: 3.47 Å) and two with sulfur atoms (S3, S4) of a neighboring molecule in the stack along the *b*-axis (Sb···S3: 3.83 Å, Sb···S4: 3.89 Å). Note that these distances, excluding the shortest Sb···S8 one, are close to or above the van der Waals Sb···S (3.80 Å) distance, indicating weaker interactions than in [SbPh(dddt)].

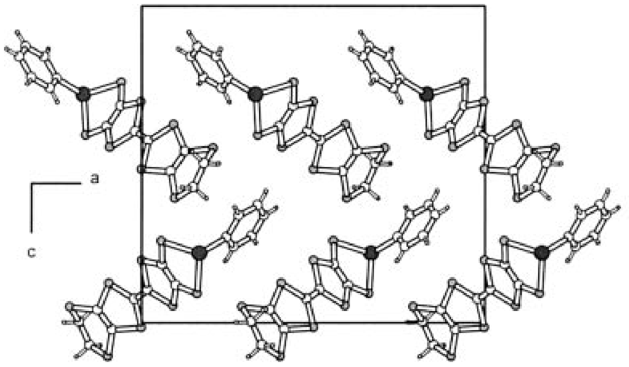


Figure 3. A view of the unit cell of (EDT-TTFS$_2$)SbPh

Table 3. Selected bond lengths (Å) and angles (°) in [SbPh(EDT-TTFS$_2$)] (**2**); symmetry transformations used to generate equivalent atoms: (a) $0.5 + x, 2 - y, z$; (b) $1 - x, 2 - y, -0.5 + z$; (c) $x, -1 + y, z$

Sb1−S1	2.450(2)	Sb1−C9	2.136(9)
Sb1−S2	2.458(2)		
Sb1···S7^a	3.852(7)	Sb1···S8^b	3.467(2)
Sb1···S3^c	3.826(2)	Sb1···S4^c	3.895(2)
C9−Sb1−S1	98.0(2)	C9−Sb1−S2	95.9(2)
S1−Sb1−S2	87.98(7)		

Electrochemical and Theoretical Studies

Cyclic voltammetry measurements were performed on complex **2** in order to determine its electrochemical behav-

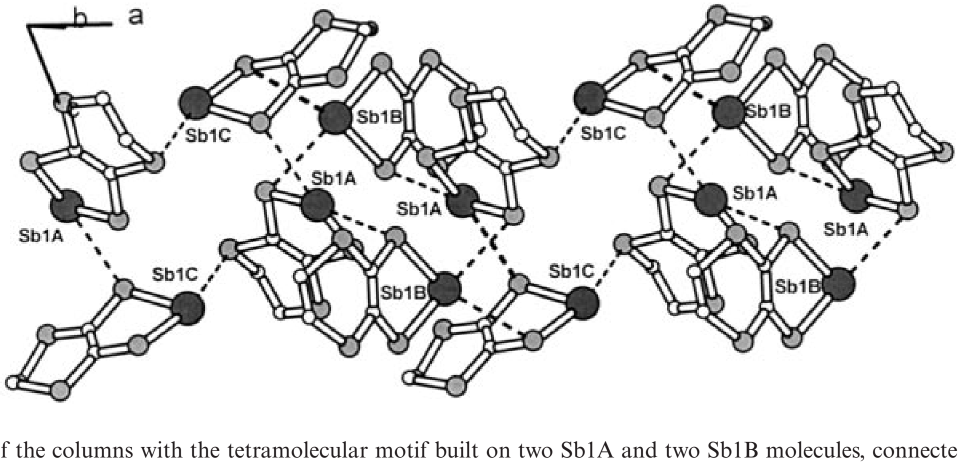


Figure 2. A view of the columns with the tetramolecular motif built on two Sb1A and two Sb1B molecules, connected together by Sb1C molecules; phenyl groups and hydrogen atoms have been omitted for clarity; Sb atoms are in dark grey, sulfur atoms in light grey

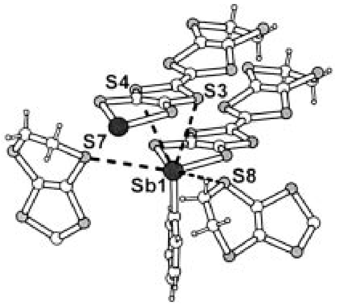


Figure 4. Detail of the coordination sphere of antimony in (EDT-TTFS$_2$)SbPh

iour and hence its potential utilization as a donor in electrocrystallization experiments. Although the two characteristic oxidation peaks, corresponding to the formation of the [**2**]$^{+\cdot}$ radical cation at E = 0.69 V (SCE) and the [**2**]$^{2+}$ dication at E = 0.89 V (SCE), are observed as expected, the overall process is only partially reversible, showing that the oxidized species of **2** is not stable in solution. This kinetic instability can be related to the flexibility of the antimony coordination sphere, leading to a multitude of ligand-scrambling reactions in solution.[25] Solutions of the neutral complex **2** in THF are also unstable, since a deposit of unidentified compounds precipitated out of the solution within one day. These observations show that the complex **2** is probably not a suitable donor for electrocrystallization experiments.

However, the complex set of intermolecular contacts identified within the crystalline structure of **2** prompted us to undertake a band-structure calculation in order to evaluate the energy gap between the valence and the conduction band of **2** along with the dispersion of these bands, thus envisaging the eventuality of an intrinsic semiconducting behavior for this compound. Indeed, previous studies dealing with the tetrakis(telluromethyl)tetrathiafulvalene (MeTe)$_4$TTF reported interesting results concerning the semiconducting properties of the compound in neutral state, very likely due to zigzag chains formed by Te···Te contacts.[32] The calculated band structure for complex **2**, represented in Figure 5, shows a valence-band built up from the HOMO of the EDT fragment, with a dispersion of about 0.2 eV. This rather weak value for the valence-band dispersion is very likely due to the absence of an antimony contribution to the HOMO of the molecule. An Sb-based HOMO would probably have led to a larger dispersion band when taking into account the numerous Sb···S intermolecular contacts. The conduction band, the dispersion of which is even weaker, also has no Sb contribution, but is exclusively formed from the empty π_4 and π_5 orbitals of the phenyl rings. Although these dispersions are somewhat slightly underestimated because of the single-ζ basis-set employed in the calculation, the bands still remain rather flat. This result, along with the gap-energy value of 1.68 eV, allows us to assess that complex **2** should be a modest semiconductor. Preliminary conductivity measurements on compressed pellets gave a σ value of about 10^{-5} S·cm^{-1}.

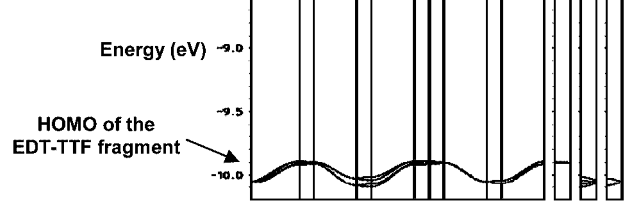


Figure 5. Calculated band structure for **2**; Γ = (0, 0, 0), R = (0.5, 0.5, 0.5), X = (0.5, 0, 0), S = (0.5, 0.5, 0), Y = (0, 0.5, 0), Z = (0, 0, 0.5), U = (0.5, 0, 0.5), T = (0, 0.5, 0.5) in units of the reciprocal lattice vectors

Experimental Section

General: The syntheses of the complexes were carried out under nitrogen, using standard Schlenk techniques. Dry toluene and hexane were obtained by distillation over Na and dry CH_2Cl_2 and CH_3CN by distillation over P_2O_5; THF was distilled from sodium/benzophenone. NMR spectra were recorded on a Bruker ARX 500 spectrometer operating at 500.04 MHz for ^{1}H and 125.75 MHz for ^{13}C. Mass spectrometry was performed on an HP 5989A spectrometer in the EI mode, with an ionization energy of 70 eV. Elemental analyses were performed by the "Service d′Analyse du CNRS" at Gif/Yvette, France. 5,6-Dihydro-[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-one,[27] EDT-TTF(SCH$_2$-CH$_2$CN)$_2$,[29,30] and phenyldichlorostibane[28] were prepared according to literature methods.

[SbPh(dddt)] (2): A solution of Me_4NOH (3.5 g 25 wt % in MeOH, 9.6 mmol) in 5 mL of THF was added to a Schlenk tube containing 5,6-dihydro-[1,3]dithiolo[4,5-*b*][1,4]dithiin-2-one (1 g, 4.8 mmol) in 30 mL of THF under magnetic stirring. A yellow precipitate appeared immediately corresponding to the formation of dddt^{2-}. After 10 min of stirring at room temperature, dichlorophenylstibane (1.3 g, 4.8 mmol) in 10 mL of THF was rapidly added. The solution became orange and a cream precipitate of tetramethylammonium chloride was formed. The suspension was stirred for 2 h and then filtered through Celite. After evaporation of the 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 0.6 g (33%). Single crystals for X-ray analysis were grown by slow evaporation of the solvent from a solution of **2** in CH_2Cl_2. ^{1}H NMR ($CDCl_3$): δ = 2.97−3.02 (m, 2 H, CH_2), 3.18−3.21 (m, 2 H, CH_2), 7.36−7.43 (m, 3 H, H *para* and *meta*), 7.60 (dd, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ = 1.4 Hz, 2 H, H *ortho*) ppm. $C_{10}H_9S_4Sb\cdot THF$: calcd. C 37.26, H 3.80; found C 37.11, H 3.71.

[SbPh(EDT-TTFS$_2$)] (2): A solution of EDT-TTF(SCH$_2$-CH$_2$CN)$_2$ (1 g, 2.15 mmol) in 40 mL of THF was treated with a solution of Me_4NOH (1.57 g, 25 wt % in MeOH, 4.3 mmol) in 10 mL of THF. An orange precipitate of EDT-TTF-S$_2^{2-}$ was formed within a few minutes and after 30 min of stirring dichlorophenylstibane (0.58 g, 2.15 mmol) in 10 mL of THF was added rapidly. The reaction mixture was stirred for 2 h, then the solvent was evaporated, the residue washed with methanol, dissolved in THF and filtered through Celite. After evaporation of THF to a small volume, MeCN was ad-

Table 4. Crystallographic data for **1** and **2**

	1	**2**
Empirical formula	$C_{10.33}H_{9.67}Cl_{0.67}S_4Sb$	$C_{14}H_9S_8Sb$
Formula mass	407.47	555.44
Crystal size (mm)	0.6 × 0.15 × 0.015	0.12 × 0.08 × 0.04
Crystal system	triclinic	orthorhombic
Space group	$P\bar{1}$	$Pca2_1$
a (Å)	12.4692(14)	18.320(4)
b (Å)	12.8323(17)	6.0582(12)
c (Å)	15.573(2)	16.983(3)
α (°)	86.452(16)	90.
β (°)	68.424(14)	90.
γ (°)	67.680(14)	90.
V (Å^3)	2134.9(5)	1884.9(7)
Z	6	4
T (K)	293(2)	293(2)
$D_{\text{calcd.}}$ (g·cm^{-3})	1.902	1.957
μ (mm^{-1})	2.343	2.343
Measured refl.	21615	10932
Unique refl.	7680	1886
Obs. refl.[a]	3510	1466
Abs. correction	numerical	multi-scan
$T_{\min}$, $T_{\max}$	0.623, 0.960	0.834, 0.889
R_{int}	0.125	0.0575
R_1 [a]	0.0446	0.031
wR_2	0.0871	0.0531
Res. density (e·Å^{-3})	+0.62, −0.54	+0.58, −0.38

The values were calculated for data with $I > 2\sigma(I)$.

ded, and then the resulting precipitate was filtered through a glass frit and dried under vacuum to yield complex **2** as a red-brown powder. Yield 0.58 g (49%). ^{1}H NMR ([D$_8$]THF): δ = 3.31 (s, 4 H, CH$_2$), 7.33 (tt, $^3J_{\text{H,H}}$ = 7.2, $^4J_{\text{H,H}}$ = 1.3 Hz, 1 H, H *para*), 7.40 (t, $^3J_{\text{H,H}}$ = 7.2 Hz, 2 H, H *meta*), 7.84 (dd, $^3J_{\text{H,H}}$ = 7.2, $^4J_{\text{H,H}}$ = 1.4 Hz, 2 H, H *ortho*) ppm. ^{13}C NMR ([D$_8$]THF): δ = 30.2 (CH$_2$), 107.7 (C=C), 113.8 (C=C), 121.4 (C=C), 128.9 (CH-*meta*), 129.8 (CH-*para*), 133.8 (CH-*ortho*), 149.0 (C-*ipso*) ppm. MS (EI): *m/z* (%) = 553, 555 (60) [M$^+$]. $C_{14}H_9S_8Sb$: calcd. C 30.27, H 1.63; found C 30.07, H 1.61.

Electrochemistry: Cyclic voltammetry experiments were performed on a VPM potentiostat in dry-THF solutions of 0.05 M nBu$_4$NPF$_6$ as electrolyte at room temperature, at a scan rate of 100 mV·s^{-1}. A Pt working electrode (diameter 1 mm), a Pt counter electrode and an SCE reference electrode were used.

Band-Structure Calculations: The tight-binding band-structure calculations were based upon the effective one-electron Hamiltonian of the extended Hückel method.[33] The off-diagonal matrix elements of the Hamiltonian were calculated according to the modified Wolfsberg−Helmholz formula.[34] All valence electrons were explicitly taken into account in the calculations, and the basis set consisted of single-ζ Slater-type orbitals, because of the higher reliability in the case of atoms with very diffuse orbitals such as antimony when compared with the double-ζ basis set.[35]

X-ray Crystallography: Crystals of [SbPh(dddt)] or [SbPh(EDT-TTFS$_2$)] were mounted on top of a thin glass fiber. Data were collected on a Stoe Imaging Plate Diffraction System (IPDS) with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). The crystal data are summarized in Table 4. Structures were solved by direct methods (SHELXS-97) and refined (SHELXL-97) by full-matrix least-squares methods. Absorption corrections were applied for both structures. Hydrogen atoms were introduced at calculated positions (riding model), included in structure factor calculations, and not refined.

CCDC-233353 (for **1**) and -233354 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] [1a] R. Williams, E. Billig, J. H. Waters, H. B. Gray, *J. Am. Chem. Soc.* **1966**, *88*, 43. [1b] G. N. Schrauzer, V. Mayweg, *J. Am. Chem. Soc.* **1962**, *84*, 3221. [1c] A. Davison, N. Edelstein, R. H. Holm, A. H. Maki, *J. Am. Chem. Soc.* **1963**, *85*, 2029.

[2] U. T. Mueller-Westerhoff, B. Vance, in *Comprehensive Coordination Chemistry* (Ed.: G. Wilkinson), Pergamon Press, Oxford, **1987**, Ch. 16.5, 595−631.

[3] T. B. Rauchfuss, *Progr. Inorg. Chem.* **2003**, *52*, 1.

[4] P. I. Clemenson, *Coord. Chem. Rev.* **1990**, *106*, 171.

[5] P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R. A. Clark, A. E. Underhill, *Coord. Chem. Rev.* **1991**, *110*, 115.

[6] A. E. Pullen, R.-M. Olk, *Coord. Chem. Rev.* **1999**, *188*, 211.

[7] M. Fourmigué, *Coord. Chem. Rev.* **1998**, *178-180*, 823.

[8] M. Hissler, J. E. McGarrah, W. B. Connick, D. K. Geiger, S. D. Cummings, R. Eisenberg, *Coord. Chem. Rev.* **2000**, *208*, 115.

[9] M. Fourmigué, *Acc. Chem. Res.* **2004**, *37*, 179.

[10] N. Le Narvor, N. Robertson, T. Weyland, J. D. Kilburn, A. E. Underhill, M. Webster, N. Svenstrup, J. Becher, *Chem. Commun.* **1996**, 1363.

[11] N. Le Narvor, N. Robertson, E. Wallace, J. D. Kilburn, A. E. Underhill, P. N. Bartlett, M. Webster, *J. Chem. Soc., Dalton Trans.* **1996**, 823.

[12] A. Kobayashi, H. Tanaka, M. Kumasaki, H. Torii, B. Narymbetov, T. Adachi, *J. Am. Chem. Soc.* **1999**, *121*, 10763.

[13] H. Tanaka, Y. Okano, H. Kobayashi, W. Suzuki, A. Kobayashi, *Science* **2001**, *291*, 285.

[14] T. Yoneda, Y. Kamata, K. Ueda, T. Sugimoto, T. Tada, M. Shiro, H. Yoshino, K. Murata, *Synth. Met.* **2003**, *135-136*, 573.

[15] [15a] R. D. McCullough, J. A. Belot, J. Seth, A. L. Rheingold, G. P. A. Yap, D. O. Cowan, *J. Mater. Chem.* **1995**, *5*, 1581. [15b] R. D. McCullough, J. A. Belot, A. L. Rheingold, G. P. A. Yap, *J. Am. Chem. Soc.* **1995**, *117*, 9913.

[16] [16a] T. Naito, N. Kobayashi, T. Inabe, *Synth. Met.* **1999**, *102*, 1687. [16b] T. Naito, N. Kobayashi, T. Inabe, *Chem. Lett.* **1998**, 723.

[17] K. Kubo, M. Nakano, H. Tamura, G.-E. Matsubayashi, *Inorg. Chim. Acta* **2002**, *336*, 120.

[18] Y. Misaki, Y. Tani, K. Takahashi, K. Tanaka, *Mol. Cryst. Liquid Cryst. Sect. A* **2002**, *379*, 71.

[19] H. Mori, M. Nakano, H. Tamura, G.-E. Matsubayashi, *J. Organomet. Chem.* **1999**, *574*, 77.

[20] R. D. McCullough, J. A. Belot, *Chem. Mater.* **1994**, *6*, 1396.

[21] K. Kubo, M. Nakano, H. Tamura, G.-E. Matsubayashi, M. Nakamoto, *J. Organomet. Chem.* **2003**, *669*, 141.

[22] K.-S. Shin, Y.-K. Han, D.-Y. Noh, *Bull. Korean Chem. Soc.* **2003**, *24*, 235.

[23] N. W. Alcock, *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 1.

[24] N. Avarvari, E. Faulques, M. Fourmigué, *Inorg. Chem.* **2001**, *40*, 2570.

[25] N. Avarvari, M. Fourmigué, *Organometallics* **2003**, *22*, 2042.

[26] A. V. Powell, S. Boissière, A. M. Chippindale, *Chem. Mater.* **2000**, *12*, 182.

[27] J. Larsen, C. Lenoir, *Synthesis* **1989**, 134.

[28] M. Nunn, D. B. Sowerby, D. M. Wesolek, *J. Organomet. Chem.* **1983**, *251*, C45.

[29] N. Svenstrup, K. M. Rasmussen, T. K. Hansen, J. Becher, *Synthesis* **1994**, 809.

[30] L. Binet, J.-M. Fabre, C. Montginoul, K. B. Simonsen, J. Becher, *J. Chem. Soc., Perkin Trans. 1* **1996**, 783.

[31] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441.

[32] [32a] H. Inokuchi, K. Imaeda, T. Enoki, T. Mori, Y. Maruyama, G. Saito, N. Okada, H. Yamochi, K. Seki, Y. Higuchi, N. Yasuoka, *Nature* **1987**, *329*, 39. [32b] J. D. Martin, E. Canadell, J. Y. Becker, J. Bernstein, *Chem. Mater.* **1993**, *5*, 1199.

[33] M. H. Whangbo, R. Hoffmann, *J. Am. Chem. Soc.* **1978**, *100*, 6093.

[34] J. H. Ammeter, H.-B. Bürgi, J. Thibeault, R. Hoffmann, *J. Am. Chem. Soc.* **1978**, *100*, 3686.

[35] T. Hughbanks, R. Hoffmann, M.-H. Whangbo, K. R. Stewart, O. Eisenstein, E. Canadell, *J. Am. Chem. Soc.* **1982**, *104*, 3876.

Received March 9, 2004
Early View Article