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Synthesis and Characterisation of Tetraethylammonium and 1,4-Dimethylpyridinium Antimony(III) Bis-dmit Complexes

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The synthesis and characterisation of two novel antimony (III) bis-dmit complexes are reported [H_2-dmit = 4,5-dimercapto-1,3-dithiole-2-thione]. Compounds [Y][Sb(dmit)$_2$] [Y = Et_4N (**1**) and Y = $C_7H_{10}N$ (1,4-dimethylpyridinium) (**2**)] are the first main group dmit complexes to show significant metal−sulfur interanionic interaction in the solid state. The [Sb(dmit)$_2$]$^-$ anions in both complexes contain strong Sb−S primary bonds arranged to give pseudo trigonal bipyramidal antimony atoms (lone pair of electrons in equatorial site; axial (Sb−S) mean 2.67 Å and equatorial (Sb−S) mean = 2.50 Å). Secondary Sb- - -S interanionic interactions have been revealed by X-ray crystallography. Details of the crystal structures are as follows **1**, monoclinic, *C*2/*c*, a = 12.391(7) Å, b = 13.090(7) Å, c = 15.587(8) Å, β = 102.7(1)°, V = 2466.3 Å^3, Z = 4; for **2**, triclinic, $P\bar{1}$, a = 8.986(5) Å, b = 10.983(6) Å, c = 11.365(6) Å, α = 87.1(1)°, β = 74.3(2)°, γ = 88.0(1)°, V = 1245.2 Å^3, Z = 2. The crystal structure of **1** consists of a polymeric two dimensional network formed by the bridging of Sb atoms and terminal S atoms of adjacent molecules. In contrast, the crystal structure of **2** consists of anionic dimers, although this structure also involves bridging between Sb atoms and terminal S atoms. In both cases the Sb- - -S interanionic distances are about 3.3 Å, which is 0.6 Å shorter than the sum of the van der Waals radii of Sb and S. Cyclic voltammetry studies of **1** in dimethylformamide show an oxidation wave and an associated reduction wave. The large separation, 0.7 V, between these is indicative of an intervening chemical reaction.

Introduction

Since the discovery of superconductivity in salts of bis-dmit nickel[1,2] and palladium[3] complexes, there has been considerable interest in the coordination chemistry of the dmit ligand [H_2-dmit = 4,5-dimercapto-1,3-dithiole-2-thione]. The structures associated with superconductivity or metallic behaviour have all contained *homosoric* stacks of bis-dmit complex anions, i.e. stacks composed of moieties of one type. In the [Me_4N][Ni(dmit)$_2$]$_2$ superconductor, the structure is two-dimensional and consists of sheets of [Ni(dmit)$_2$] pairs along the (110) direction, with intermolecular S- - -S contacts as short as 3.49 Å along the *b* direction.[1] [TTF][Ni(dmit)$_2$]$_2$ and α- and α′-[TTF][Pd(dmit)$_2$]$_2$ (TTF$^{\bullet+}$ = tetrafulvalenium radical cation) are isostructural and their structures consist of segregated stacks of the TTF and [M(dmit)$_2$] moieties.[2,3] They have a quasi-three-dimensional network of intermolecular S- - -S interactions between [M(dmit)$_2$] units and also between TTF and [M(dmit)$_2$] units. High conductivity is usually associated with partial oxidation states with nominal Ni and Pd oxidation states of +3.5 in the superconducting dmits.

Most studies have addressed dmit complexes of the late transition metals: however, there has also been some interest in main group dmit complexes. Mono-, bis-, and tris-dmit complexes of Sn(IV) have been prepared,[4−6] and tris-dmit complexes of In(III) and Tl(III) have also been reported.[7] Intramolecular coordinations of 4, 5, 6, and 8 have been observed; however, no significant intermolecular coordination has been reported to date. In this study we have investigated dmit complexes of antimony. Antimony is a particularly

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[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1995.

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Table 1. Crystallographic Data for **1** and **2**

	1	**2**
chem formula	$C_{14}H_{20}NS_{10}Sb$	$C_{13}H_{10}NS_{10}Sb$
fw	644.13	621.94
space group	*C*2/*c*	$P\bar{1}$
a, A	12.391(7)	8.986(5)
b, A	13.090(7)	10.983(6)
c, A	15.587(8)	11.365(6)
α, deg	90	87.1(1)
β, deg	102.7(1)	74.3(2)
γ, deg	90	88.0(1)
V, A^3	2466.3	1245.2
Z	4	2
ϱ_c, g cm^{-3}	1.75	1.92
T, °C	25	25
λ, Å	0.71073	0.71073
μ (Mo-Kα), cm^{-1}	18.80	20.67
$R(F_o)^a$	0.059	0.038
$R_w(F_o)^a$	0.066	0.039

[a] $R(F_o) = \Sigma(||F_o| - |F_o||)/\Sigma|F_o|$ and $R_w(F_o) = [\Sigma w(|F_o| - |F_o|^2]/\Sigma[w|F_o|^2]^{1/2}$.

Table 2. Fractional Coordinates with Equivalent Isotropic Thermal Parameters

atom	*x*	*y*	*z*	U_{eq},[a] Å^2
		Anion of **2**		
Sb	0.41064(7)	0.73374(6)	0.80930(6)	0.0409(2)
S(1)	0.2680(3)	0.9125(2)	0.9191(2)	0.0459(9)
S(2)	0.5990(3)	0.9085(2)	0.6818(2)	0.056(1)
S(3)	0.6376(3)	1.1603(2)	0.7560(2)	0.0505(9)
S(4)	0.3707(3)	1.1579(2)	0.9616(2)	0.049(1)
S(5)	0.5729(4)	1.3780(2)	0.9159(3)	0.068(1)
S(6)	0.1405(3)	0.6293(2)	0.9105(2)	0.0477(9)
S(7)	0.3147(3)	0.7404(2)	0.6195(2)	0.046(1)
S(8)	0.0268(3)	0.6733(2)	0.5652(2)	0.0475(9)
S(9)	−0.1302(3)	0.5932(2)	0.8111(2)	0.0470(9)
S(10)	−0.2979(3)	0.5862(3)	0.6163(3)	0.056(1)
C(1)	0.404(1)	1.0274(8)	0.8746(8)	0.039(4)
C(2)	0.532(1)	1.0262(8)	0.7785(8)	0.043(4)
C(3)	0.530(1)	1.2392(9)	0.8807(9)	0.055(4)
C(4)	0.059(1)	0.6410(8)	0.7866(8)	0.039(4)
C(5)	0.1310(9)	0.6792(8)	0.6723(8)	0.039(3)
C(6)	−0.1413(9)	0.6161(8)	0.6622(8)	0.042(4)
		Anion of **1**		
Sb	0.000000	0.646260(1)	0.250000	0.5020(6)
S1	0.0040(2)	0.5258(2)	0.1266(2)	0.0452(13)
S2	0.2173(2)	0.6088(2)	0.2917(2)	0.0487(15)
S3	0.1683(2)	0.3853(2)	0.0825(2)	0.0645(17)
S4	0.3497(2)	0.4517(2)	0.2203(2)	0.0466(13)
S5	0.3954(3)	0.3009(3)	0.0882(2)	0.0878(21)
C1	0.1393(8)	0.4797(7)	0.1520(6)	0.0494(53)
C2	0.2237(7)	0.5128(6)	0.2190(7)	0.0454(51)
C3	0.3081(9)	0.3751(8)	0.1295(7)	0.0654(71)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

promising template metal because it exhibits significant long-range coordination in its sulfides and it has two readily accessible oxidation states, facilitating orbital overlap between dmits in bis-dmit complexes. Here we report the first synthesis of complexes of the $[Sb(dmit)_2]^-$ anion and the first main group dmit salts showing significant intermolecular coordination.

Experimental Section

Synthesis. Melting points were measured on a Kofler hot-stage and are uncorrected. NMR spectra were run on a Bruker 250 MHz instrument, IR spectra on a Philips Analytical PU9800 FTIR instrument and UV spectra on a Perkin-Elmer Lambda 15 UV−vis spectrophotometer. The solid state NMR was obtained by the SERC solid-state NMR service at Durham University, Durham, England. The compounds $[Et_4N]_2[Zn(dmit)_2]$ and $[C_7H_{10}N]_2[Zn(dmit)_2]$ were prepared according to published procedure.[8]

Preparation of $[Et_4N][Sb(dmit)_2]$ (1). A solution of $NaSCN.2H_2O$ (0.351 g, 3 mmol) in acetone (20 cm^3) was added to a solution of $SbBr_3$ (0.361 g, 1 mmol) in acetone (20 cm^3). After thorough mixing, a solution of $[Et_4N]_2[Zn(dmit)_2]$ (0.719 g, 1 mmol) in acetone (30 cm^3) was gradually added to the cloudy solution of $Sb(SCN)_3$. Reaction occurred immediately as shown by the color change. Solvent was removed and crude product was recrystallized from acetone to give black crystalline blocks. Mp: 180−182 °C. Anal. Calcd for $C_{14}H_{20}NS_{10}Sb$: C, 26.1; H, 3.1; N, 2.2. Found: C, 25.9; H, 2.8; N, 2.2. ^1H NMR (acetone-d_6, 250 MHz): δ 1.4 (tt, 12H, CH_3), 3.5 (q, 8H, CH_2N). ^{13}C NMR (DMSO-d_6, 62.9 MHz): δ 8.7 (CH_3), 53.0 (NCH_2), 133.9 (C=C), 213.2 (C=S). ^{13}C NMR (solid state, 75.4 MHz): δ 7.8 (CH_3), 52.8 (NCH_2), 129.1, 140.7 (C=C), 210.5 (C=S). IR (KBr): 2975, 1478, 1433, 1167, 1047, 1026, 994, 880, 775 cm^{-1}.

Preparation of $[C_7H_{10}N][Sb(dmit)_2]$ (2). This was prepared analogously to **1**. $[C_7H_{10}N]_2[Zn(dmit)_2]$ was prepared from 4-dimethylpyridinium iodide. Recrystallization of the crude $[C_7H_{10}N][Sb(dmit)_2]$ from acetone gave dark green crystalline blocks. Mp: 167−168 °C. Anal. Calcd for $C_{13}H_{10}NS_{10}Sb$: C, 25.1; H, 1.6; N, 2.2. Found: C, 24.8; H, 1.6; N, 2.2. ^1H NMR (acetone-d_6, 250 MHz δ 3.3 (s, 3H, C−CH_3), 4.6 (s, 3H, N−CH_3), 8.1 (d, 2H, H3), and 9.0 (d, 2H, H2) (aryl-H's). ^{13}C NMR (solid state, 75.4 MHz): δ 23.9 (C−CH_3), 49.0 (N−CH_3), 127.3, 139.6, 144.4, 159.3 (C=C), 210.2 (C=S). IR (KBr): 3040, 2924, 2853, 1638, 1431, 1049, 1026, 880, 812 cm^{-1}.

Crystal Structure Determination. Crystal data, data collection and processing details for compounds **1** and **2** are presented in Table 1. Data were obtained with a Philips PW-100 four-circle diffractometer with graphite monochromator Mo Kα radiation (λ = 0.710 73 Å). Intensity data were collected at 25 °C using 2θ scan method. Two reference reflections, monitored periodically, showed no significant variation in intensity. Data were corrected for Lorentz and polarization effects and, in both refinements, empirical absorption correction was applied to the intensities.

The positions of Sb and S atoms were determined from the three-dimensional Patterson function. The remaining non-hydrogen atoms were located from successive difference Fourier maps using SHELX-76.[9a] Atomic scattering factors were taken from ref 9b. Hydrogen atoms were located and given ideal positions. Anisotropic thermal parameters were used for all non-hydrogen atoms, except for the $[Et_4N]^+$ cations. Blocked-cascade least-squares refinement converged to R = 0.059 for **1** and R = 0.038 for **2**.

Cyclic Voltammetric Studies. All electrochemical measurements were performed by using a Sycopel Autostat Scientific voltammeter. The electrochemical cell used for cyclic voltammetry employed a platinum working electrode, a platinum wire as the auxiliary electrode and a 10^{-1} M solution of $Ag/AgNO_3$ in CH_3CN (acetonitrile), as reference electrode. Measurements were carried out on a 10^{-3} M solution of **1** in DMF (dimethylformamide), containing a 10^{-1} M solution of Et_4NClO_4 as the supporting electrolyte. Argon was passed through the solution prior to taking the measurments, and an argon blanket was maintained above the solutions during experiments.

Results and Discussion

Crystal and Molecular Structures of 1 and 2. Atomic coordinates for the anions of **1** and **2** are listed in Table 2, bond lengths in Table 3 and bond angles in Table 4. The basic geometries involving the Sb atom and the two dmit ligands in **1** and **2** are very similar. The $[Sb(dmit)_2]^-$ anions, in both cases, contain four strong intraanionic Sb−S bonds arranged in a pseudo trigonal bipyramidal array about Sb, with a lone pair occupying an equatorial site. The mean $(Sb-S)_{axial}$ and the mean $(Sb-S)_{equatorial}$ bond lengths are 2.67 and 2.50 Å,

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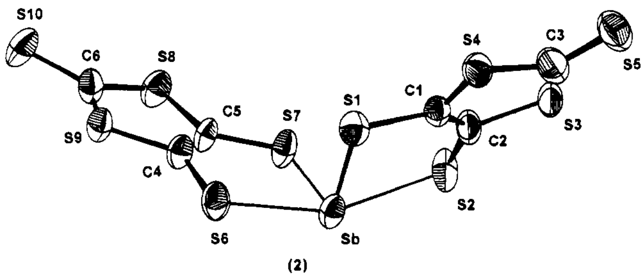
Table 3. Selected Bond Distances (Å)

	Compound **1**		
Sb(1)–S(1)	2.496(3)	Sb(1)–S(2)	2.672(3)
S(1)–C(1)	1.74(1)	S(2)–C(2)	1.71(1)
S(3)–C(1)	1.73(1)	S(2)–C(3)	1.73(1)
S(4)–C(2)	1.75(1)	S(4)–C(3)	1.72(1)
S(5)–C(3)	1.68(1)	C(1)–C(2)	1.38(1)
Sb- - -S(5″)	3.27(3)		
	Compound **2**		
Sb–S(1)	2.502(4)	Sb–S(2)	2.696(4)
Sb–S(6)	2.661(4)	Sb–S(7)	2.527(3)
S(1)–C(1)	1.744(9)	S(2)–C(2)	1.724(9)
S(3)–C(2)	1.750(9)	S(3)–C(3)	1.74(1)
S(4)–C(1)	1.754(9)	S(4)–C(3)	1.73(1)
S(5)–C(3)	1.680(9)	S(6)–C(4)	1.75(1)
S(7)–C(5)	1.743(8)	S(8)–C(5)	1.730(9)
S(8)–C(6)	1.733(8)	S(9)–C(4)	1.739(9)
S(9)–C(6)	1.73(1)	S(10)–C(6)	1.68(1)
C(1)–C(2)	1.36(1)	C(4)–C(5)	1.34(1)
Sb- - -S(5′)	3.30(5)		

Table 4. Selected Bond Angles (deg)

	Compound **1**		
S(1)–Sb–S(2)	83.2(1)	S(2′)–Sb–S(2)	158.8(2)
Sb–S(2)–C(2)	99.5(4)	S(2′)–Sb–S(1)	83.5(1)
C(2)–S(4)–C(3)	98.7(5)	Sb–S(1)–C(1)	103.0(3)
S(3)–C(1)–C(2)	118.2(7)	C(1)–S(3)–C(3)	96.7(5)
S(4)–C(2)–C(1)	113.1(7)	S(1)–C(1)–S(3)	115.2(6)
S(2)–C(2)–S(4)	120.1(6)	S(1)–C(1)–C(2)	126.6(8)
S(3)–C(3)–S(5)	123.4(4)	S(2)–C(2)–C(1)	126.7(8)
S(1′)–Sb–S(1)	101.6(1)	S(4)–C(3)–S(5)	123.4(7)
S(1)–Sb- - -S(5″)	155.9(2)	S(3)–C(3)–S(4)	113.2(7)
S(2)–Sb- - -S(5‴)	120.5(2)	S(5″)- - -Sb- - -S(5‴)	103.5(2)
S(1)–Sb- - -S(5‴)	82.4(2)	S(2)–Sb- - -S(5″)	73.6(2)
	Compound **2**		
S(6)–Sb–S(7)	82.9(2)	S(2)–Sb–S(7)	82.5(1)
S(2)–Sb–S(6)	155.6(2)	S(1)–Sb–S(7)	101.5(2)
S(1)–Sb–S(6)	81.3(2)	S(1)–Sb–S(2)	82.6(2)
Sb–S(1)–C(1)	102.3(4)	Sb–S(2)–C(2)	98.1(4)
C(2)–S(3)–C(3)	99.5(5)	C(1)–S(4)–C(3)	98.4(5)
Sb–S(6)–C(4)	100.1(3)	Sb–S(7)–C(5)	103.1(3)
C(5)–S(8)–C(6)	97.4(5)	C(4)–S(9)–C(6)	97.1(5)
S(1)–C(1)–S(4)	117.0(6)	S(4)–C(1)–C(2)	116.6(8)
S(1)–C(1)–C(2)	126.4(8)	S(3)–C(2)–C(1)	114.2(8)
S(2)–C(2)–C(1)	127.0(8)	S(2)–C(2)–S(3)	118.8(6)
S(4)–C(3)–S(5)	124.4(7)	S(3)–C(3)–S(5)	124.4(7)
S(3)–C(3)–S(4)	111.2(6)	S(6)–C(4)–S(9)	117.9(5)
S(9)–C(4)–C(5)	116.4(8)	S(6)–C(4)–C(5)	125.7(8)
S(8)–C(5)–C(4)	115.5(8)	S(7)–C(5)–C(4)	127.8(8)
S(7)–C(5)–S(8)	116.6(5)	S(9)–C(6)–S(10)	123.8(6)
S(8)–C(6)–S(10)	122.7(6)	S(8)–C(6)–S(9)	113.5(6)
S(1)–Sb- - -S(5′)	86.6(2)	S(2)–Sb- - -S(5′)	123.2(2)
S(7)–Sb- - -S(5′)	154.1(2)	S(6)–Sb- - -S(5′)	73.7(2)



(2)

Figure 1. Atomic arrangement and numbering scheme for the anions of **1** and **2**.

respectively. Figure 1 shows the molecular structure and numbering system for the anion [Sb(dmit)$_2$]$^-$ for **1** and **2**. In **1** the anionic units are located on a 2-fold axis. However the anions of **1** and **2** are also involved in secondary and interanionic interactions between antimony and the thiocarbonyl sulfur atoms. In **1**, intermolecular contacts between each Sb atom and two C=S units in adjacent molecules at ca. 3.3 Å, result in a polymeric network (Figure 2). In **2**, the anions are linked into dimeric units *via* Sb- - -S contacts of also ca. 3.3 Å (Figure 3). These Sb- - -S interanionic distances are about 0.6 Å shorter than the sum of the van der Waals radii of Sb and S.[10]

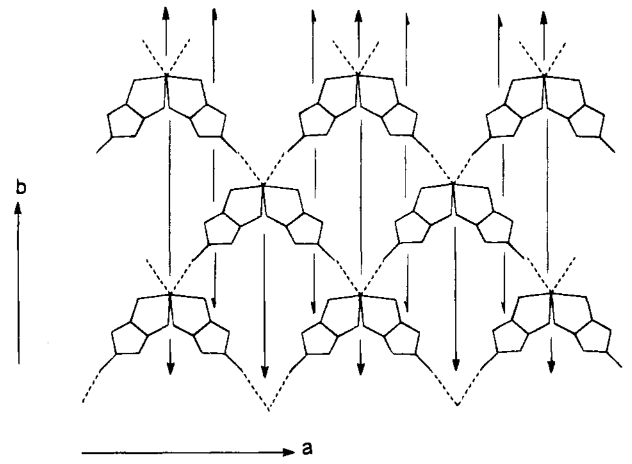


Figure 2. Projection of the anion of **1** onto the *ab* plane.

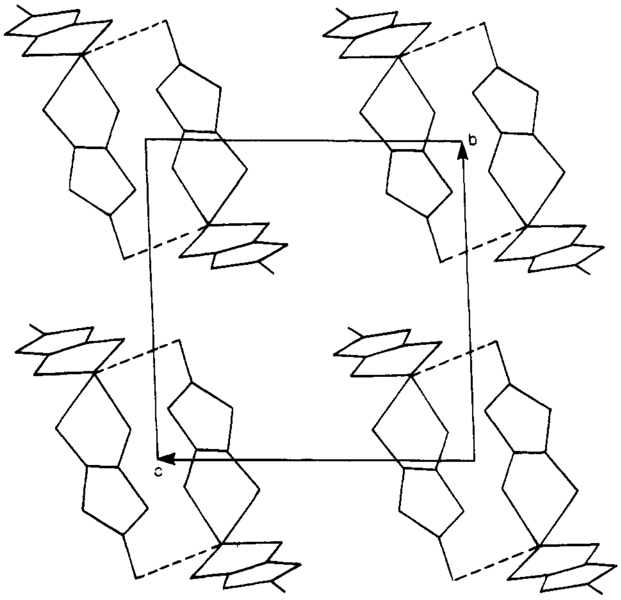


Figure 3. Projection of the anion of **2** onto the *bc* plane.

Considering both the primary and secondary bonding, the Sb atom in **1** is 6-coordinate with each metal atom chelated by two dmit ligands and bridged by two thione groups of adjacent molecules. The polymeric layers so formed are parallel to the *ab* plane and alternate with planes of cations at interlayer separation of 3.8 Å ($d_{002}/2$). The shortest intermolecular contact distances between anions of successive layers range within 3.5–3.6 Å. The array about each Sb atom displays the symmetry C_2 imposed by the space group; it arises from an octahedral geometry which is distorted in the presence of stereochemically active lone pair. The most appropriate description for the array about Sb in **1** is a distorted pentagonal bipyramid with one of the equatorial positions occupied by the stereochemically active lone pair. The sulfur atoms S(2) and S(2′) occupy the axial positions, while the equatorial positions are occupied by S(1), S(1′), S(5″), S(5‴), and the lone pair, presumably directed along the C_2 axis between S(5″) and S(5‴) (Figure 1). Gillespie[11] predicted a pentagonal bipyramidal structure (a "1:5:1" arrange-

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[10] Spackman, M. A. *J. Chem. Phys.* **1986**, *11*, 85 and references therein.
[11] Gillespie, R. J. *Can. J. Chem.* **1960**, *38*, 818.

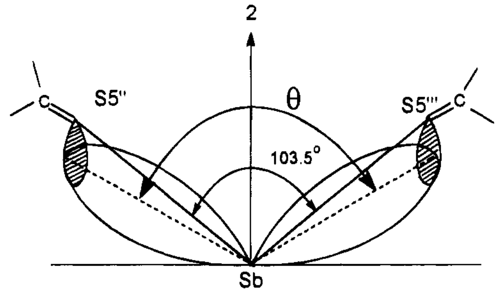

Figure 4. Overlap of Sb orbitals with S=C orbitals.

ment) for AX_6E (where A = nontransition element, X = ligand atom, and E = lone pair). The arrangement in **1** is however somewhat distorted away from a regular pentagonal bipyramidal arrangement; for example atoms S(1), S(1′), S(5″), S(5‴), and Sb are not coplanar. The bond angles involving S(5″) and S(5‴) may be better assessed with reference to the direction of the hybrid orbitals of Sb [which overlap the orbitals of S(5″) and S(5‴)] rather than with the Sb- - -S(5″) and Sb- - -S(5‴) directions (Figure 4). This will render, for example, a greater S(5″)- - -Sb- - -S(5‴) bond angle (angle θ in Figure 4) than the value measured of 103.5°—possibly to a value approaching that expected for a near-pentagonal geometry in the equatorial girdle, which also includes the antimony lone pair. The sum of the angles subtended by the equatorial atoms at antimony in **1** is 369.9°. A less distorted pentagonal bipyramidal geometry about the central metal atom has been found in the tetraphenylarsonium bis(1,2-dicyanoethene-1,2-dithiolato)bismuthate(III), which has also four sulfur atoms and the lone pair in equatorial sites. In this linear polymeric chained complex, the four primary Bi−S bonds are in the range 2.664(7)−2.836(8) Å, and the two secondary Bi- - -S bonds are between 3.182(10) and 3.238(10).[12] In this complex, the sum of the angles subtended by the equatorial atoms at bismuth is 364.2°, with the bismuth deviation of −0.02 Å from the least squares equatorial plane; the axial S−Bi−S is 159.8(6)°. As illustrated in Figure 3, the dimeric units in **2** are linked by two weak Sb- - -S bonds per dimer with the Sb atoms becoming 5-coordinate, if the secondary interactions are taken into account. The geometry in **2** is essentially distorted pseudooctahedral with an equatorial lone pair. The presence of bond angles of less than 90° in AX_5E type complexes, such as **2**, can be attributed to the strong repulsion exerted by the lone pair of electrons in an octahedral arrangement of six pairs (Table 4).

Cyclic Voltammetry. Three peaks were observed in the cyclic voltammetry of $[Et_4N][Sb(dmit)_2]$ in DMF (Figure 5). When scanning was performed anodically from 0 V vs Ag/Ag^+, an oxidation peak (O1) and a postpeak (O2), indicating of strong adsorption of reactant, were observed at about 0.4 V. The peak current of O2 showed a v^1 dependence (where v is the scan speed), further confirming it as an adsorption peak.[13] On the reverse scan a reduction peak was observed at about −0.3 V. When scanning was performed cathodically from 0 V, no reduction peak was observed. For scan rates of 30 mV s^{-1} and above, the peak current ratio $i_{\mathrm{p_{R1}}}/i_{\mathrm{p_{O1}}}$ was close to unity. The large peak separations between $E_{\mathrm{p_{R1}}}$ and $E_{\mathrm{p_{O1}}}$ of ca. 0.7V and the large values obtained for the slopes $d(E_p)/d(\log v)$ of about 0.14 V for all the observed peaks are consistent with chemical reactions following each electrochemical step. Thus, the mechanism could be described as a ECEC process. The chemical reactions most likely entail a change in solvation of the dmit complex, as more severe chemical reactions would not give rise to a value of unity for $i_{\mathrm{p_a}}/i_{\mathrm{p_c}}$ for such low scan rates. The crystal structures presented in this study show that the starting complex, $[Sb(dmit)_2]^-$, has a tendency to maximize its coordination. On oxidation to the neutral $Sb(dmit)_2$ species, the coordination environment is likely to rearrange perhaps by losing a coordinating solvent molecule.

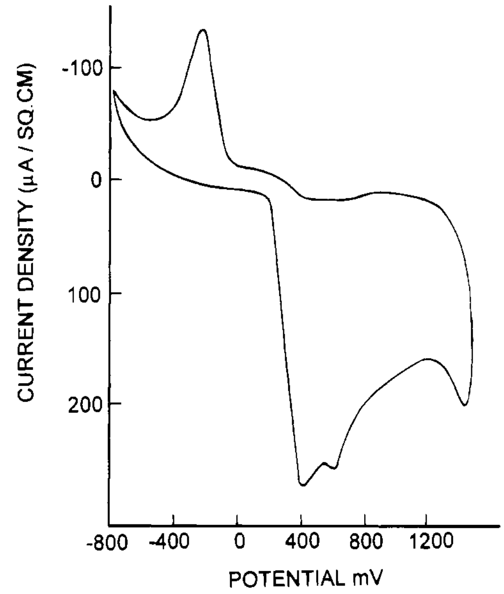

Figure 5. Cyclic voltammogram of **1**.

Conclusion

The first main group dmit complexes that show metal-sulfur interaction in the solid state have been reported. $[Et_4N][Sb(dmit)_2]$ (**1**) exhibits a polymeric two-dimensional network whereas [1,4-dimethylpyridinium]$[Sb(dmit)_2]$ (**2**) forms anionic dimers. Although **1** does show favorable intermolecular coordination for electron conductivity, four-terminal dc measurements on a single crystal indicated that it was at best a poor semiconductor.

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Supporting Information Available: Full list of crystallographic data (Table S1) and, for compound 1, bond distances (Table S2), bond angles (Table S3), fractional coordinates of all non-H atoms (Table S4), fractional coordinates of H atoms (Table S5) and thermal parameters (Table S6), and, for compound 2, bond distances (Table S7), bond angles (Table S8), fractional coordinates of all non-H atoms (Table S9), fractional coordinates of H atoms (Table S10), and thermal parameters (Table S11) (9 pages). Ordering information is given on any current masthead page.

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