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Syntheses, characterizations and crystal structures of new organoantimony(V) complexes with heterocyclic (S, N) ligand

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Abstract

Eight new organoantimony(V) complexes with 1-phenyl-1H-tetrazole-5-thiol [L^1H] and 2,5-dimercapto-4-phenyl-1,3,4-thiodiazole [L^2H] of the type R_nSbL_{5-n} (L = L^1: $n = 4$, R = n-Bu **1**, Ph **2**, $n = 3$, R = Me **3**, Ph **4**; L = L^2: $n = 4$, R = n-Bu **5**, Ph **6**, $n = 3$, R = Me **7**, Ph **8**) have been synthesized. All the complexes **1**–**8** have been characterized by elemental, FT-IR, ^{1}H and ^{13}C NMR analyses. Among them complexes **2**, **6** and **8** have also been confirmed by X-ray crystallography. The structure analyses show that the antimony atoms in complexes **2** and **6** display a trigonal bipyramid geometry, while it displays a distorted capped trigonal prism in complex **8** with two intramolecular Sb···N weak interactions. Furthermore, the supramolecular structure of **2** has been found to consist of one-dimensional linear molecular chain built up by intermolecular C–H···N weak hydrogen bonds, while a macrocyclic dimer has been found in complex **6** linked by intermolecular C–H···S weak hydrogen bonds with head-to-tail arrangement. Interestingly, one-dimensional helical chain is recognized in complex **8**, which is connected by intermolecular C–H···S weak hydrogen bonds.
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Keywords: 1-Phenyl-1H-tetrazole-5-thiol; 2,5-Dimercapto-4-phenyl-1,3,4-thiodiazole; Organoantimony(V); Crystal structure; Weak hydrogen bond

1. Introduction

Metal-based drugs have been increasingly researched due to their certain advantages over purely organic compounds in drug therapy [1–3]. Among them, antimony complexes have been reported with good cytotoxicity and antitumor activities [3], especially Takahashi et al. have reported some antimony complexes can affect the repair of DNA-double strand break [3c]. However, until now most of the studies have been focused on the inorganic antimony and organoantimony(III) complexes [4], few organoantimony(V) complexes have been reported [5]. To fill the gap, we selected two interesting heterocyclic ligands – 1-phenyl-1H-tetrazole-5-thiol and 2,5-dimercapto-4-phenyl-1,3,4-thiodiazole – to react with organoantimony(V) compounds.

The two ligands are interesting because both of them are derived from heterocyclic thiones that contain at least one deprotonated heterocyclic thioamide group $(N–C–S)^-$ and can act as monodentate, chelating and bridging ligands, which has been extensively studied in the field of transition-metal coordination chemistry [6]. In our previous work, we have studied the detailed coordination chemistry of this type of ligands in organotin and organongermanium complexes, the structure analyses revealed that the coordination mode of these ligands varied dramatically according to distinct R groups of the precursor R_nMCl_{4-n} (M = Sn, Ge) [7]. As regards the organoantimony(V) compounds, however, the situation is rather ambiguous, since no X-ray crystallography have authenticated organoantimony(V) compounds with heterocyclic thiones so far. From a theoretical point of view, we think it is necessary to do an initial probe in the coordination chemistry of organoantimony(V) complexes with heterocyclic (S, N) ligands, thus we report here some details of the syntheses

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of a series of organoantimony(V) complexes of the type R_nSbL_{5-n} (L = L^1: $n = 4$, R = n-Bu **1**, Ph **2**; $n = 3$, R = Me **3**, Ph **4**; L = L^2: $n = 4$, R = n-Bu **5**, Ph **6**; $n = 3$, R = Me **7**, Ph **8**) and characterize them by elemental, IR and ^{1}H and ^{13}C NMR analyses. X-ray crystallography analyses of the complexes **2**, **6** and **8** have also been given in present paper.

2. Experimental

2.1. Materials and measurements

All reagents and solvents were purchased commercially and used without further purification unless otherwise noted. The melting points were obtained with Kofler micro melting point apparatus and were uncorrected. Infrared spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs and sodium chloride optics. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX-300 spectrometer operating at 300 and 75.3 MHz, respectively. The chemical shifts were reported in ppm with respect to the references and were stated relative to tetramethylsilane (TMS) for ^{1}H and ^{13}C NMR. Elemental analyses were performed with a PE-2400II apparatus.

2.2. Syntheses of the complexes 1–8

2.2.1. (n-Bu)₄Sb[S(C₇H₅N₄)] (1)

The reaction was carried out under nitrogen atmosphere. The 1-phenyl-1H-tetrazole-5-thiol (0.178 g, 1 mmol) and sodium ethoxide (0.068 g, 1 mmol) were added to the solution of absolute benzene (20 ml) in a Schlenk flask and stirred for 0.5 h. The tetra-n-butylantimony bromide (0.430 g, 1 mmol) was then added to the reactor, the reaction mixture was stirred for 12 h at 40 °C and then filtrated. The filtered solution was gradually removed by evaporation under vacuum until the solid product was obtained. Yield: 82%; m.p. 198–200 °C. Anal. Calc. for C₂₃H₄₁N₄SSb: C, 52.38; H, 7.84; N, 10.62; S, 6.08. Found: C, 52.30; H, 7.85; N, 10.65; S, 6.00%. IR (KBr, cm^{-1}): 3035, 2930, 2855, 1605, 973, 690, 475, 365. ^{1}H NMR (CDCl₃): 7.68 (d, 2H, o-Ph–N), 7.48 (m, 3H, m,p-Ph–N), 1.58–1.35 (m, 24H, CH_2CH_2CH_2), 0.85 (d, 12H, CH_3(CH₂)₃) ppm. ^{13}C NMR (CDCl₃): 156.8 (C–S), 134.7 (i-C₆H₅–N), 129.5 (p-C₆H₅–N), 129.2 (m-C₆H₅–N), 124.1 (o-C₆H₅–N), 27.8 (β-C), 26.0 (γ-C), 16.5 (α-C), 12.8 (δ-C).

2.2.2. Ph₄Sb[S(C₇H₅N₄)] · C₆H₆ (2)

Complex **2** was prepared in the same way of **1**, by adding tetraphenylantimony bromide (0.510 g, 1 mmol) to the 1-phenyl-1H-tetrazole-5-thiol (0.178 g, 1 mmol) and sodium ethoxide (0.068 g, 1 mmol) in benzene (20 ml). Buff crystals of **2** suitable for X-ray diffraction were obtained from mother liquid. Yield: 87%; m.p. 210–212 °C. Anal. Calc. for C₃₇H₃₁N₄SSb: C, 64.83; H, 4.56; N, 8.17; S, 4.68. Found: C, 64.85; H, 4.52; N, 8.23; S, 4.70%. IR (KBr, cm^{-1}): 3030, 2928, 2852, 1600, 975, 484, 358. ^{1}H

NMR (CDCl₃): δ 7.78 (d, 8H, o-Ph–Sb), 7.52–7.44 (m, 23H, m,p-Ph–Sb, o,m,p-C₆H₅–N) 7.28 (s, 6H, C₆H₆) ppm. ^{13}C NMR (CDCl₃): 156.0 (C–S), 135.2 (i-C₆H₅–N), 135.0 (i-Ph–Sb), 134.8 (m-Ph–Sb), 129.0 (m-Ph–N), 128.8 (p-C₆H₅–N), 128.4 (p-Ph–Sb), 127.9 (o-Ph–Sb), 124.5 (o-Ph–N).

2.2.3. Me₃Sb[S(C₇H₅N₄)]₂ (3)

Complex **3** was prepared in the same way of **1**, by adding trimethylantimony dichloride (0.119 g. 0.5 mmol) to the 1-phenyl-1H-tetrazole-5-thiol (0.178 g, 1 mmol) and sodium ethoxide (0.068 g, 1 mmol) in benzene (20 ml). Yield: 85%; m.p. 178–180 °C. Anal. Calc. for C₁₇H₁₉N₈S₂Sb: C, 39.17; H, 3.67; N, 21.50; S, 12.30. Found: C, 39.20; H, 3.66; N, 21.55; S, 12.27%. IR (KBr, cm^{-1}): 3028, 2925, 2856, 1573, 977, 690, 478, 428, 352. ^{1}H NMR (CDCl₃): δ 7.60 (d, 2H, o-Ph–N), 7.45 (m, 3H, m,p-Ph–N), 1.02 (s, 9H, Me–Sb) ppm. ^{13}C NMR (CDCl₃): 156.5 (C–S), 134.3 (i-C₆H₅–N), 129.6 (p-C₆H₅–N), 129.4 (m-C₆H₅–N), 124.5 (o-C₆H₅–N), 8.8 (Me–Sb).

2.2.4. Ph₃Sb[S(C₇H₅N₄)]₂ (4)

Complex **4** was prepared in the same way of **1**, by adding triphenylantimony dichloride (0.212 g. 0.5 mmol) to the 1-phenyl-1H-tetrazole-5-thiol (0.178 g, 1 mmol) and sodium ethoxide (0.068 g, 1 mmol) in benzene (20 ml). Yield: 89%; m.p. 188–190 °C. Anal. Calc. for C₃₂H₂₅N₈S₂Sb: C, 54.33; H, 3.56; N, 15.84; S, 9.06. Found: C, 54.30; H, 3.60; N, 15.77; S, 9.05%. IR (KBr, cm^{-1}): 3025, 2930, 2858, 1580, 970, 688, 482, 432, 368. ^{1}H NMR (CDCl₃): δ 7.72 (d, 6H, o-Ph–Sb), 7.50 (d, 4H, o-Ph–N), 7.48–7.33 (m, 24H, m,p-Ph–Sb, m,p-C₆H₅–N) ppm. ^{13}C NMR (CDCl₃): 156.8 (C–S), 138.0(i-Ph–N), 135.5 (i-Ph–Sb), 134.3 (m-Ph–Sb), 129.3 (m-Ph–N), 128.0 (p-Ph–N), 126.8 (p-Ph–Sb), 125.5 (o-Ph–N).

2.2.5. (n-Bu)₄Sb[S(C₈H₅N₂S₂)] (5)

Complex **5** was prepared in the same way of **1**, by adding tetra-n-butylantimony bromide (0.430 g, 1 mmol) to potassium salt of 2,5-dimercapto-4-phenyl-1,3,4-thiodiazole (0.264 g, 1 mmol) in benzene (20 ml). Yield: 83%; m.p. 195–197 °C. Anal. Calc. for C₂₄H₄₁N₂S₃Sb: C, 50.08; H, 7.18; N, 4.87; S, 16.71. Found: C, 50.12; H, 7.20; N, 4.83; S, 16.70. IR (KBr, cm^{-1}): 3015, 2975, 2868, 1608, 1252, 977, 698, 480, 368. ^{1}H NMR (CDCl₃): δ 7.65 (d, 2H, o-Ph–N), 7.42 (m, 3H, m,p-C₆H₅–N), 1.75–1.42 (m, 24H, CH_2CH_2CH_2) 0.85 (d, 12H, CH_3(CH₂)₃) ppm. ^{13}C NMR (CDCl₃): δ 187.3 (C–S), 158.3 (C=S), 138.4 (i-Ph–N), 128.5 (m,p-Ph–N), 125.8 (o-Ph), 28.5 (β-C), 26.8 (γ-C), 16.1 (α-C), 13.4 (δ-C).

2.2.6. Ph₄Sb[S(C₈H₅N₂S₂)] (6)

Complex **6** was prepared in the same way of **1**, by adding tetraphenylantimony bromide (0.510 g, 1 mmol) to potassium salt of 2,5-dimercapto-4-phenyl-1,3,4-thiodiazole (0.264 g, 1 mmol) in benzene (20 ml). Yellow crystals of **6** suitable for X-ray diffraction were obtained from

benzene. Yield: 89%; m.p. 205–207 °C. Anal. Calc. for $C_{32}H_{25}N_2S_3Sb$: C, 58.63; H, 3.84; N, 4.27; S, 14.67. Found: C, 58.68; H, 3.88; N, 4.25; S, 14.60%. IR (KBr, cm^{-1}): 3058, 1593, 1246, 968, 488, 371. ^{1}H NMR (CDCl$_3$): δ 7.68 (d, 8H, o-Ph–Sb), 7.42–7.28 (m, 17H, m,p-Ph–Sb, o,m,p-C$_6$H$_5$–N) ppm. ^{13}C NMR (CDCl$_3$): δ 186.8 (C–S), 157.8 (C=S), 137.6 (i-Ph–N), 136.5 (i-Ph–Sb), 136.2 (m-Ph–Sb), 130.0 (m-Ph–N), 128.9 (p-Ph–N), 128.4 (p-Ph–Sb), 127.9 (o-Ph–Sb), 125.5 (o-Ph–N).

2.2.7. Me₃Sb[S(C₈H₅N₂S₂)]₂ (7)

Complex **7** was prepared in the same way of **1**, by adding trimethylantimony dichloride (0.119 g. 0.5 mmol) to potassium salt of 2,5-dimercapto-4-phenyl-1,3,4-thiodiazole (0.264 g, 1 mmol) in benzene (20 ml). Yield: 88%; m.p. 168–170 °C. Anal. Calc. for $C_{19}H_{19}N_4S_6Sb$: C, 36.95; H, 3.10; N, 9.07; S, 31.15. Found: C, 36.90; H, 3.15; N, 9.10; S, 31.10%. IR (KBr, cm^{-1}): 3060, 1578, 1256, 982, 688, 478, 425, 362. ^{1}H NMR (CDCl$_3$): δ 7.70 (d, 6H, o-Ph–N), 7.45 (m, 6H, m,p-C$_6$H$_5$–N), 1.05 (s, 9H, Me–Sb) ppm. ^{13}C NMR (CDCl$_3$): δ 187.0 (C–S), 158.0 (C=S), 138.2 (i-Ph–N), 129.4 (m,p-Ph–N), 125.5 (o-Ph), 8.5 (Me–Sb).

2.2.8. Ph₃Sb[S(C₈H₅N₂S₂)]₂ (8)

Complex **8** was prepared in the same way of **1**, by adding triphenylantimony dichloride (0.212 g. 0.5 mmol) to potassium salt of 2,5-dimercapto-4-phenyl-1,3,4-thiodiazole (0.264 g, 1 mmol) in benzene (20 ml). Yield: 90%. Yellow crystals of **8** suitable for X-ray diffraction were

obtained from hexane/dichloromethane; m.p. 195–197 °C. Anal. Calc. for $C_{34}H_{25}N_4S_6Sb$: C, 50.81; H, 3.14; N, 6.97; S, 23.94. Found: C, 50.85; H, 3.10; N, 6.95; S, 23.90%. IR (KBr, cm^{-1}): 3050, 1581, 1248, 973, 678, 472, 438, 355. ^{1}H NMR (CDCl$_3$): δ 7.78 (d, 6H, o-Ph–Sb), 7.59 (d, 4H, o-Ph–N), 7.52–7.38 (m, 24H, m,p-Ph–Sb, m,p-C$_6$H$_5$–N) ppm. ^{13}C NMR (CDCl$_3$): δ 185.6 (C–S), 158.1 (C=S), 138.2 (i-Ph–N), 135.9 (i-Ph–Sb), 134.6 (m-Ph–Sb), 129.0 (m-Ph–N), 128.2 (p-Ph–N), 127.0 (p-Ph–Sb), 125.8 (o-Ph–N).

2.3. X-ray crystallographic studies

Crystals were mounted in Lindemann capillaries under nitrogen. All X-ray crystallographic data were collected on a Bruker SMART CCD 1000 diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 298 (2) K. A semi-empirical absorption correction was applied to the data. The structure was solved by direct methods using SHELXS-97 and refined against F^2 by full-matrix least squares using SHELXL-97. Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations are listed in Table 1.

3. Results and discussion

3.1. Syntheses of the complexes 1–8

The synthesis procedure is given in Scheme 1.

Table 1
Crystal and refinement data for complexes **2**, **6** and **8**

Complex	**2**	**6**	**8**
Empirical formula	$C_{37}H_{31}N_4SSb$	$C_{32}H_{25}N_2S_3Sb$	$C_{34}H_{25}N_4S_6Sb$
Formula weight	685.47	655.47	803.69
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
Unit cell dimensions			
a (Å)	11.4791(19)	16.652(4)	10.143(3)
b (Å)	12.118(2)	19.537(4)	8.953(3)
c (Å)	13.437(2)	18.371(4)	37.825(3)
α (°)	77.441(2)	90	90
β (°)	66.304(2)	104.944(4)	94.166(2)
γ (°)	77.166(2)	90	90
Volume (Å^3)	1651.5(5)	5774(2)	3426.1(15)
Z	2	8	4
D_{cal} (Mg m^{-3})	1.378	1.508	1.558
Crystal size (mm)	$0.45 \times 0.38 \times 0.22$	$0.39 \times 0.22 \times 0.13$	$0.43 \times 0.38 \times 0.22$
F(000)	696	2640	1616
Absorption coefficient (mm^{-1})	0.929	1.197	1.202
Data/restraints/parameters	5765/0/388	10163/0/685	6039/0/406
θ Range for data collection (°)	1.67–25.03	1.80–25.02	2.16–25.03
Goodness-of-fit	1.000	1.024	1.001
Final R indices [$I > 2\sigma (I)$]	$R_1 = 0.0284$	$R_1 = 0.0447$	0.0472
	$wR_2 = 0.0659$	$wR_2 = 0.0739$	0.0992
R indices (all data)	$R_1 = 0.0382$	$R_1 = 0.1138$	0.0841
	$wR_2 = 0.0730$	$wR_2 = 0.0987$	0.1135
Largest diff. peak and hole (e Å^{-3})	0.645 and −0.371	0.825 and −0.751	0.667 and −0.479

Scheme 1.
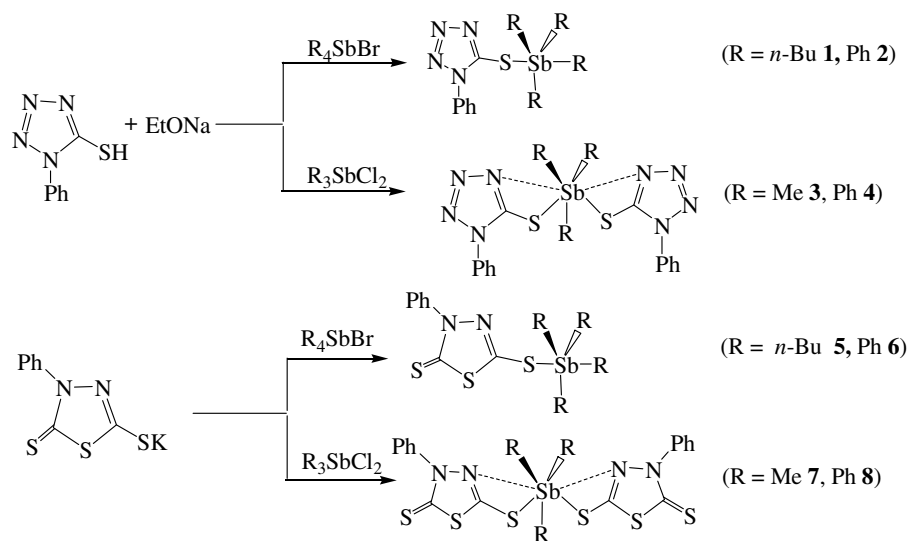
3.2. IR spectroscopic studies of the complexes 1–8

The explicit feature in the IR spectra of the eight complexes 1–8 is the absence of the band in the region 2550–2430 cm^{-1} (for L^{1}H) and 2530–2420 cm^{-1} (for L^{2}H), which appear in the free ligands as the –SH vibration, indicating metal–ligand bond formation through this site. In the far-IR spectra, the absorption around 360 cm^{-1} region for all complexes 1–8, which is absent in the spectra of the ligands, may be assigned to Sb–S stretching mode of the vibration [8] and these data further supports the formation of Sb–S bond in complexes 1–8. In addition, the Sb–C absorption values are found between 472 and 488 cm^{-1} in all the complexes, which are consistent with that reported in other organoantimony complexes [9,10].

It is worthy to note that besides the absorption region belonging to Sb–S, there is another weak band at about 430 cm^{-1} in complexes 3, 4, 7 and 8 that can be attributed to Sb···N vibration according to the literature [11,12]. Furthermore, the absorption band of C=N in complexes 3, 4, 7 and 8 all shift about 20 cm^{-1} towards high-frequency compared with those of complexes 1, 2, 5 and 6, which also prove that there exist the weak coordination from nitrogen atom of the ligands to antimony atoms in complexes 3, 4, 7 and 8. As a result, the probable geometry for complexes 3, 4, 7 and 8 can be described as a capped trigonal prism. The following crystal structure of complex 8 well supports such a conclusion.

3.3. ^{1}H and ^{13}C NMR data of the complexes 1–8

The ^{1}HNMR data show that the signal of the –SH proton in the spectra of the two ligands are both absent in all of the complexes, indicating the removal of the –SH proton and the formation of Sb–S bonds. The formation accords well with what the IR data have revealed. Moreover, the ^{1}H NMR chemical shifts of the phenyl group (Sb–C$_6$H$_6$)

in complexes 2, 4, 6 and 8 7.28–7.78 ppm, and those of methyl or methylene connected directly with antimony in complexes 1, 3, 5 and 7, 1.02–1.75 ppm, upfield shift as compared with those of their corresponding precursors, indicating there may exist novel coordination of the ligand to antimony atom for all the eight complexes 1–8. Signals for the other groups appear at the same position as in the ligands.

The structural changes occurring in ligands upon deprotonation and coordination to the Sb atom should be reflected by the changes in the ^{13}C NMR spectra of complex 1–8. If the ligands chelate Sb through thiolate form, C–S should be further low frequency in the spectra of all complexes compared with those in free ligands. As shown above, the chemical shifts in all complexes 1–8 are downshifted about 10 ppm compared with the free ligand, indicating that the ligands involved in these complexes act as thiolate form. All the above analyses are also confirmed by crystal structure of complex 2, 6 and 8.

3.4. Crystal structures of complexes 2, 6 and 8

Molecular and supramolecular structures of complexes 2, 6 and 8 and are shown in Figs. 1–6, respectively; and the selected bond lengths and angles for complexes 2, 6 and 8 and are given in Tables 2–4, respectively.

3.4.1. Ph$_4$Sb[S(C$_7$H$_5$N$_4$)] · C$_6$H$_6$ and Ph$_4$Sb[S(C$_8$H$_5$N$_2$S$_2$)]

For complex 2, the component Ph$_4$Sb[S(C$_7$H$_5$N$_4$)] co-crystallizes with a benzene molecule but it has not been found the obvious interaction between the Ph$_4$Sb[S(C$_7$H$_5$N$_4$)] moiety and the solvent molecule. For complex 6, the asymmetric unit contains two crystallographically independent molecules A and B. Conformations of the two independent molecules are almost the same, with only little differences in bond lengths and bond angles (see Table 3). The molecular struc-
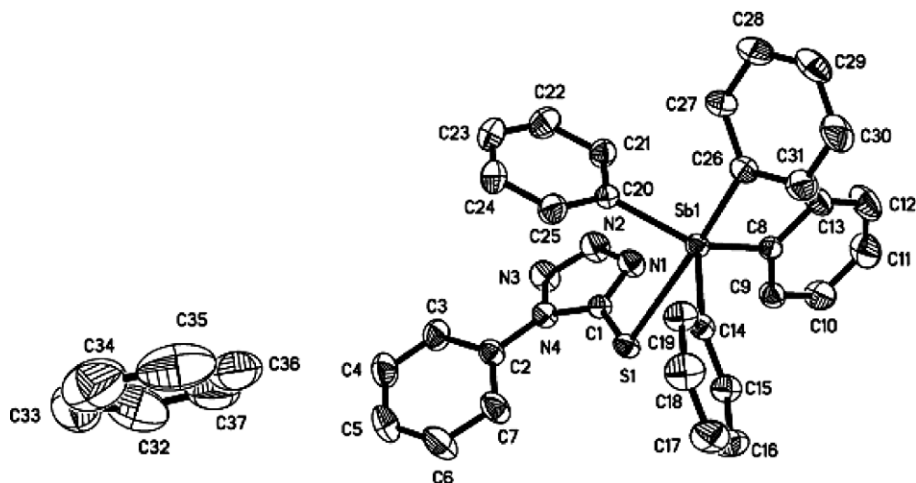
Fig. 1. Molecular structure of complex 2, ellipsoids at 30% probability.
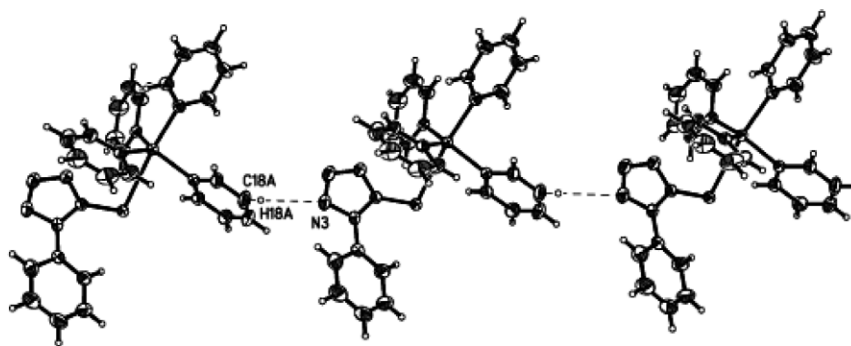
Fig. 2. Supramolecular structure of complex 2, showing 1D linear molecular chain linked by intermolecular C–H···N weak hydrogen bonds.
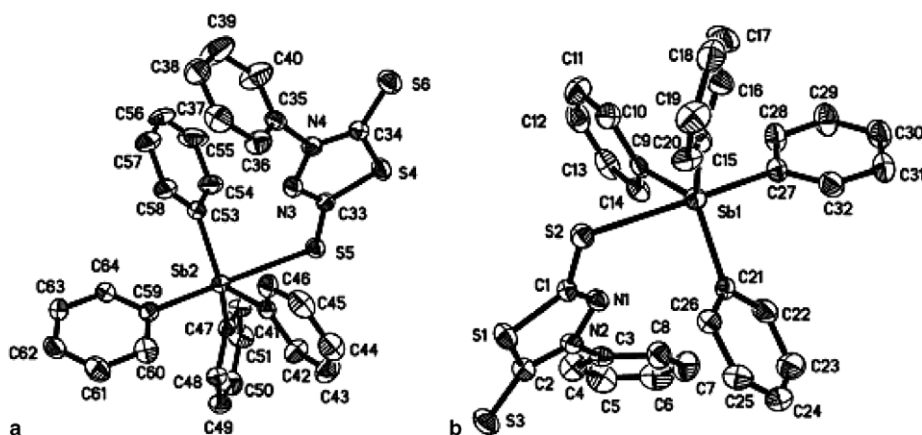
Fig. 3. Molecular structure of complex 6, ellipsoids at 30% probability.

tures of complexes 2 and 6 are basically the same except for bonding with different ligands (L^1 for 2 and L^2 for 6), and the coordination environments of central antimony atoms in both complexes are five-coordinated with a trigonal bipyramidal geometry. Three phenyl groups occupy the equatorial plane and the fourth phenyl group and the thiol atom from ligand lie in axial sites. The sum of equatorial angles are 355.52° (C8–Sb1–C14 114.26(11)°, C8–Sb1–C20

121.90(11)°, C14–Sb1–C20 119.36(11)°) in complex 2, and 356.6° (C9–Sb1–C15 112.8(3)°, C9–Sb1–C21 129.7(2)°, C15–Sb1–C21 114.1(2)°) and 355.1° (C41–Sb2–C47 111.8(2)°, C41–Sb2–C53 125.4(3)°, C47–Sb2–C53 117.9(3)°) in complex 6, and the corresponding axial–Sb–axial angles are 171.50(8)° (C26–Sb1–S1) in complex 2, and 178.59(18)° (C27–Sb1–S2) and 179.2(2)° (C59–Sb2–S5) in complex 6, suggesting both of them are close to the ideal trigonal
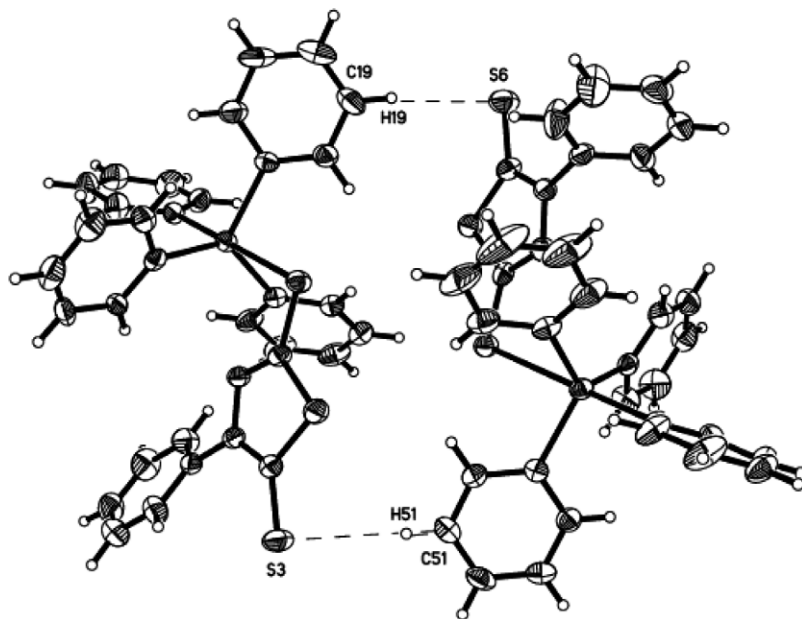
Fig. 4. Macrocyclic dimer of complex **6**, showing intermolecular C–H···S weak hydrogen bonds.
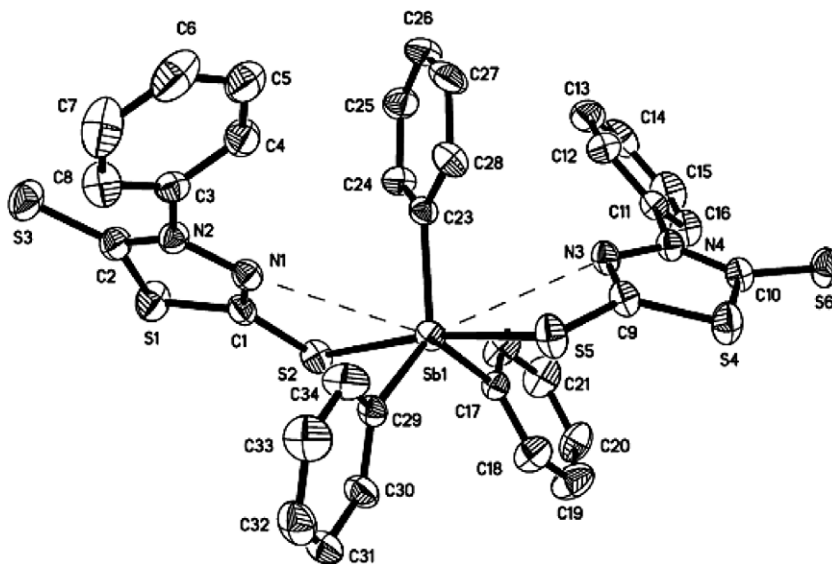

Fig. 5. Molecular structure of complex **8**, ellipsoids at 30% probability.

bipyramidal geometry. The axial Sb–C in complexes **2** and **6** (Sb1–C26, 2.159(3) Å for **2**, Sb1–C27 2.179(6) Å and Sb2–C59 2.166(6) Å for **6**) are slightly larger than the average value of the equatorial Sb–C bond (2.111 Å for **2**, 2.115 and 2.113 Å for **6**), which is consistent with that found in another five-coordinated trigonal bipyramidal organoantimony complex, $Ph_3Sb[S_2C_2(CN)_2]$ [13]. The Sb–S bond lengths, Sb1–S1 (2.8762(8) Å) for complex **2**, Sb1–S2 (2.8999(17) Å) and Sb2–S5 (2.9248(17) Å) for complex **6**, are slightly longer that found in (2-mercaptopyridine-*N*-oxide-*O,S*)-tetraphenyl-antimony ethanol solvate (2.716 Å) [14] but much shorter than the sum of van der Waals radii of Sb and S atoms, 4.05 Å. The long distance between Sb

and N atoms in complex **2** (3.711 Å), even longer than the van der Waals radii of Sb and N atoms (3.70 Å), suggests there is no apparent intramolecular Sb···N interaction found in this complex. For complex **6**, although the distance between Sb and N atoms (3.388 and 3.407 Å) are shorter than that found in **2**, all the spectra of complex **6** show that no apparent Sb···N interaction have been found, so we can reasonably think that both the Sb atoms in complexes **2** and **6** are five-coordinated and there are no markedly differences between their geometries.

Interestingly, there is a linear molecular chain found in crystal lattice of complex **2** (Fig. 2), which is linked by intermolecular C18–H18···N3 weak hydrogen bonds. The
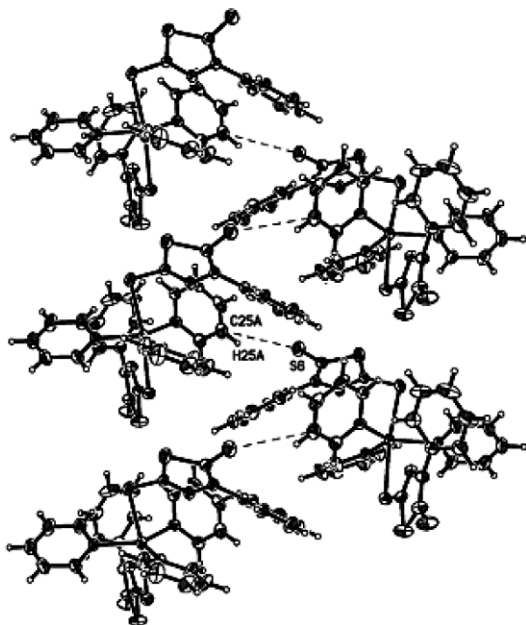
Fig. 6. Supramolecular structure of complex **8**, showing a helical chain along the *b*-axis linked by intermolecular C–H···S weak hydrogen bonds.

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

Bond lengths (Å)			
Sb1–C8	2.122(3)	Sb1–C14	2.108(3)
Sb1–C20	2.114(3)	Sb1–C26	2.159(3)
Sb1–S1	2.8762(8)		
Bond angles (°)			
C8–Sb1–C14	114.26(11)	C8–Sb1–C20	121.90(11)
C14–Sb1–C20	119.36(11)	C26–Sb1–S1	171.50(8)
C8–Sb1–C26	97.17(11)	C14–Sb1–C26	96.67(11)
C20–Sb1–C26	97.31(11)	C14–Sb1–S1	77.69(8)
C8–Sb1–S1	90.99(8)	C20–Sb1–S1	80.27(8)

Table 3
Selected bond lengths (Å) and angles (°) for the complex **6**

Bond lengths (Å)			
Sb1–C9	2.115(6)	Sb1–C15	2.099(6)
Sb1–C21	2.135(6)	Sb1–C27	2.179(6)
Sb2–C41	2.095(6)	Sb2–C47	2.111(6)
Sb2–C53	2.113(7)	Sb2–C59	2.166(6)
Sb1–S2	2.8999(17)	Sb2–S5	2.9248(17)
Bond angles (°)			
C9–Sb1–C15	112.8(3)	C9–Sb1–C21	129.7(2)
C9–Sb1–C27	96.0(2)	C15–Sb1–C21	114.1(2)
C15–Sb1–C27	97.2(2)	C21–Sb1–C27	95.2(2)
C9–Sb1–S2	82.62(15)	C15–Sb1–S2	82.94(17)
C21–Sb1–S2	85.99(16)	C27–Sb1–S2	178.59(18)
C41–Sb2–C47	111.8(2)	C41–Sb2–C53	125.4(3)
C41–Sb2–C59	99.1(2)	C47–Sb2–C53	117.9(3)
C47–Sb2–C59	98.1(2)	C53–Sb2–C59	95.3(3)
C41–Sb2–S5	80.09(16)	C47–Sb2–S5	82.17(16)
C53–Sb2–S5	85.26(18)	C59–Sb2–S5	179.2(2)

Table 4
Selected bond lengths (Å) and angles (°) for the complex **8**

Bond lengths (Å)			
Sb1–C17	2.097(5)	Sb1–C23	2.118(5)
Sb1–C29	2.108(4)	Sb1–S5	2.5851(17)
Sb1–S2	2.6107(17)	Sb1–N1	3.245(4)
Sb1–N3	3.291(4)		
Bond angles (°)			
C17–Sb1–C23	114.24(19)	C17–Sb1–C29	119.6(2)
C23–Sb1–C29	126.14(19)	C17–Sb1–S2	84.83(15)
C23–Sb1–S2	93.77(15)	C29–Sb1–S2	90.07(15)
C23–Sb1–S5	94.65(15)	C17–Sb1–S5	93.47(15)
C29–Sb1–S5	83.40(15)	S2–Sb1–S5	171.36(5)
C17–Sb1–N1	137.48(17)	C23–Sb1–N1	69.23(16)
C29–Sb1–N1	71.01(15)	C17–Sb1–N3	66.02(16)
C23–Sb1–N3	69.18(16)	C29–Sb1–N3	135.24(16)
S2–Sb1–N1	52.97(9)	N1–Sb1–S5	129.03(9)
N3–Sb1–S5	52.07(8)	S2–Sb1–N3	133.64(8)
N1–Sb1–N3	138.26(11)		

values of C18A···N3, H18A···N3 and C18A–H18A···N3 are 2.616 Å, 3.412 Å and 143.79°, respectively. For complex **6**, a pair of intermolecular C–H···S (C19–H19···S6 and C51–H51···S3) weak hydrogen bonds have been recognized (C19···S6 3.755 Å, H19···S6 2.917 Å, C19–H19···S6 150.58°; C51···S3 3.853 Å, H51···S3 2.936 Å, C51–H51···S3 168.34), which associate the two discrete molecules into an interesting macrocyclic dimer (Fig. 4).

For complex **8**, the central Sb atom is bonded by three phenyl groups and two sulfur atoms from two [S(C$_8$H$_5$N$_2$S$_2$)]$^-$ moiety, thus it displays a distorted trigoanl bipyramidal geometry. Three phenyl groups occupy the equatorial plane with a "paddle-wheel" model and two ligands are in axial positions with asymmetric model to lessen the spatial hindrance from the bulky phenyl groups. The sum of equatorial angles is 359.98° (C17–Sb1–C23 114.24(19)°, C17–Sb1–C29 119.6(2)°, C23–Sb1–C29 126.14(19)°), and the corresponding axial–Sb–axial is 171.36(5)° (S2–Sb1–S5). The three Sb–C bond lengths around Sb atom in the equatorial plane show no apparent difference (Sb1–C17 2.097(5) Å, Sb1–C23 2.118(5) Å, Sb1–C29 2.108(4) Å). The two Sb–S bond lengths (Sb1–S2 2.6107(17) Å, Sb1–S5 2.5851(17) Å), which are slightly shorter than that found in complexes **2** and **6**, are in the normal rang of that reported in triphenylantimony thiolates (2.469–2.689 Å) [13,14]. Besides, two intramolecular Sb···N weak interactions (Sb1···N1 3.245(4) Å and Sb1···N3 3.291(4) Å) have been recognized between Sb1 atom and N1, N3 atoms, which are much shorter than the sum of van der Waals radii of Sb and N atoms, 3.70 Å. And these intramolecular Sb···N weak interactions were also supported by the spectra of complex **8**. If the two weak Sb···N interactions are also considered, the geometry of Sb1 can be best described as distorted capped trigonal prism. It is noteworthy that the two Sb···N are of 3.245(4) Å (Sb1···N1) and 3.291(4) Å (Sb1···N3), which are markedly elongated compared to those reported in 1,1,1-triphenyl-1λ^5-stiba-2,4,-tithia-3,5-dizazcyclopenta-2,

4-diene (2.489 Å) [15] and tetramethyl-(8-oxyquinolinato)-antimony (2.464 Å) [16], so it is obvious that the Sb···N coordination interactions in complex **8** are very weak.

The supramolecular structure of complex **8** is dominated by one-dimensional helical polymer (Fig. 6) along the *b*-axis linked by intermolecular C–H···S (C25A···S6 = 3.799 Å, H25A···S6 = 2.972 Å, C25A–H25A···S6 = 148.82°) weak hydrogen bonds, which is similar to that found in our previous reported organotin complex [17]. The 'pitch' of the helix (8.953 Å) is also close to that found in $[(Ph_3Sn)_2(SC_6H_4CO_2)]\cdot 2EtOH$ (9.991 Å) [17] but much shorter than in 4-[2-(triethylstannyl)terazole-5-yl-pyridine (40 Å) [18].

4. Conclusions

In summary, a series of organoantimony(V) complexes based on 1-phenyl-1H-tetrazole-5-thiol and 2,5-dimercapto-4-phenyl-1,3,4-thiodiazole ligands containing heterocyclic S,N donors have been synthesized and characterized. Detailed studies on the structures and spectra of these complexes indicate that there exists such an inclination that the structures of those tetraalkylantimony complexes **1**, **2**, **5** and **6** are apt to be of trigonal bipyramid geometry and those trialkylantimony complexes **3**, **4**, **7** and **8** are likely to construct capped trigonal prism geometry with weak Sb···N weak interactions.

The tendency to form intramolecular Sb···N weak interactions in theses complexes appears that $R_3Sb(Ligand)_2$ complexes are stronger than $R_4Sb(Ligand)$ complexes, which is not surprising in view of the fact that the similar situation have also been found in other organometal complexes with these ligands [19]. This seems to be defined by the Lewis acidity of antimony center, and it must also reflect the availability of the antimony d orbitals for bonding, since the increase in number of highly electronegative atom or groups approaching metal, results in a considerable contraction of the otherwise high-energy and diffuse metal d orbitals, allowing thus a better metal–ligand overlap [20]. In the present case, such electronegative atoms are the nitrogen atoms adjacent to the bonded sulfur atoms, thus the more heterocyclic ligands bind to antimony and the stronger are the intramolecular Sb···N interactions.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 293422, 274956 and 274955 for complexes **2**, **6** and **8**, respectively. Copies of these information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.Ac.uk or www:http://www.ccdc.cam.ac.uk).

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