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Synthesis and Structure of Tetraphenylantimony *N*,*N*-Diethyldithiocarbamate

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Abstract—Tetraphenylantimony chloride was reacted with sodium *N*,*N*-diethyldithiocarbamate in water to obtain tetraphenylantimony *N*,*N*-diethyldithiocarbamate in 98% yield. According to X-ray diffraction data, the configuration of the molecule of tetraphenylantimony diethyldithiocarbamate is distorted octahedron, and the Sb–S bond lengths are 2.705(2) and 2.771(2) Å.

The synthesis and structure of many oxygen-containing aryl compounds of pentavalent antimony of the general formula Ar_4SbX (where X is an oxygen-containing radical) have been described [1–4]. Analogous derivatives of antimony with sulfur-containing ligands X have never been obtained.

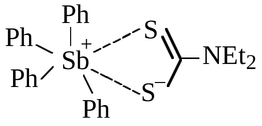
We found tetraphenylantimony chloride with reacts with sodium *N*,*N*-diethyldithiocarbamate in water to give tetraphenylantimony *N*,*N*-diethyldithiocarbamate $Ph_4SbSC(S)NEt_2$ (**I**).

$$Ph_4SbCl + NaSC(S)NEt_2 \longrightarrow Ph_4SbSC(S)NEt_2 + NaCl.$$

Attempted synthesis of triphenylantimony bis(*N*,*N*-diethyldithiocarbamate) from triphenylantimony dichloride and sodium *N*,*N*-diethyldithiocarbamate in toluene at elevated temperature did not give the target product. Instead, reduction of triphenylantimony dichloride to triphenylstibine and dimerization of *N*,*N*-diethyldithiocarbamate groups took place.

$$Ph_3SbCl_2 + 2NaSC(S)NEt_2 \longrightarrow Ph_3Sb + [SC(S)NEt_2]_2 + 2NaCl.$$

According to X-ray diffraction data, the antimony atom in compound **I** has a distorted octahedral coordination (Fig. 1). The Sb–S bonds are strongly lengthened [2.705(2) and 2.771(2) Å, Table 2], because they are evidently coordination in nature. Hence, complex **I** can be characterized by the following resonance structure.



Note that the inequality of the Sb–S distances and the reverse redistribution of the C–S bond lengths (longer Sb–S distance relates to shorter C–S bond) provide further evidence for this resonance structure. The geometry of the diethyldithiocarbamate group shows that the nitrogen lone pair is conjugated with the C=S bond (the nitrogen atom has a planar trigonal coordination, the S_2CN fragment is planar, and the $C^1–N^1$ bond is strongly shortened). The crystal packing of compound **I** is mainly determined by dispersion interactions (Fig. 2).

EXPERIMENTAL

The IR spectra were recorded on a Hitachi-215 spectrometer for suspensions in Vaseline oil between sodium chloride plates.

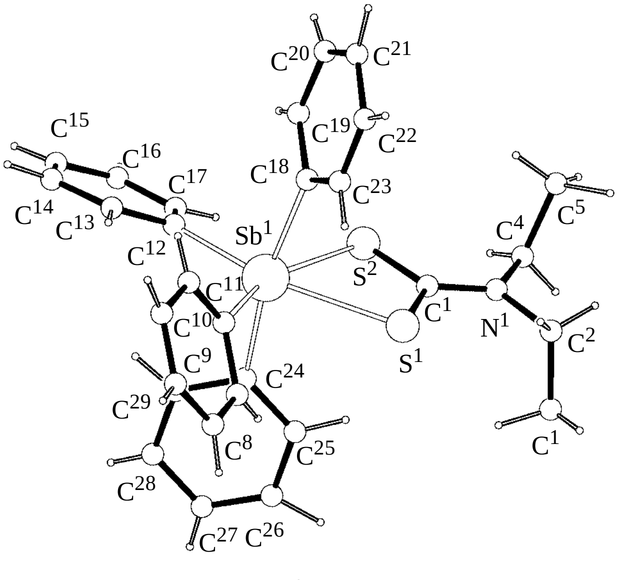


Fig. 1. Geometry of complex **I** in crystal.

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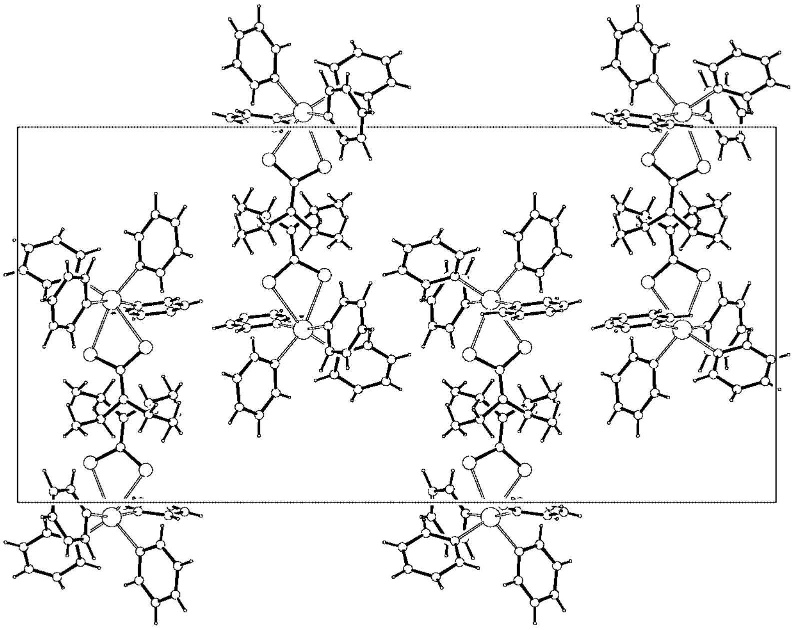

Fig. 2. Crystal packing of molecules **I** as viewed along the 0*y* axis.

Table 1. Bond lengths (*d*, Å) and bond angles (ω, deg) in structure **I**

Bond	*d*, Å	Bond	*d*, Å
$Sb^1–S^1$	2.705(2)	$S^1–C^1$	1.717(7)
$Sb^1–S^2$	2.771(2)	$S^2–C^1$	1.706(7)
$Sb^1–C^6$	2.161(6)	$N^1–C^1$	1.330(8)
$Sb^1–C^{12}$	2.160(6)	$N^1–C^2$	1.481(9)
$Sb^1–C^{18}$	2.170(7)	$N^1–C^4$	1.457(9)
$Sb^1–C^{24}$	2.197(7)		
Angle	ω, deg	Angle	ω, deg
$S^1Sb^1S^2$	65.50(6)	$C^{12}Sb^1C^{18}$	94.4(2)
$S^1Sb^1C^6$	94.1(2)	$C^{12}Sb^1C^{24}$	91.8(2)
$S^1Sb^1C^{12}$	160.7(2)	$C^{18}Sb^1C^{24}$	168.5(2)
$S^1Sb^1C^{18}$	83.0(2)	$Sb^1S^1C^1$	88.3(2)
$S^1Sb^1C^{24}$	87.9(2)	$Sb^1S^2C^1$	86.3(2)
$S^2Sb^1C^6$	159.6(2)	$C^1N^1C^2$	121.3(5)
$S^2Sb^1C^{12}$	95.3(2)	$C^1N^1C^4$	123.1(5)
$S^2Sb^1C^{18}$	83.4(2)	$C^2N^1C^4$	115.6(5)
$S^2Sb^1C^{24}$	86.4(2)	$S^1C^1S^2$	119.8(4)
$C^6Sb^1C^{12}$	105.1(2)	$S^1C^1N^1$	119.2(5)
$C^6Sb^1C^{18}$	94.8(2)	$S^2C^1N^1$	121.0(5)
$C^6Sb^1C^{24}$	92.9(2)		

X-ray diffraction analysis of crystals of tetraphenylantimony *N,N*-diethyldithiocarbamate (I). $C_{29}H_{30}NS_2Sb$. The unit cell parameters and the intensities of 5749 reflections, 2212 of which had $I > 2\sigma$, were measured on an Enraf–Nonius CAD-4 automatic four-curcle *K*-diffractometer at 20°C (MoK_α radiation, λMoK_α 0.71073 Å, graphite monochromator, ω/2θ scanning, $\theta < 29.96°$). Rhombic crystals; at 20°C, *a* 16.820(3), *b* 9.455(3), *c* 33.934(9) Å, *V* 5397(3) Å^3, *Z* 8, d_{calc} 1.42 g/cm^3. Space group *Pbca*. Empirical absorption corrections (μMo 11.93 cm^{-1}) were included. The structure was solved by the direct method by the SIR program [5] and refined first isotropically and then anisotropically. Hydrogen atoms were located by difference synthesis and refined isotropically in the final stage to *R* 0.033 and R_W 0.037 on 2079 unique reflections with $F^2 > 3\sigma$. The atomic coordinates are listed in Table 1, and the principal geometric parameters, in Table 2. All calculations were carried out by means of the MolEN complex of programs [6] on DEC Alpha Station. Analysis of molecular contacts and molecular drawings were performed be means of the WINPL98 program [7].

Tetraphenylantimony *N,N*-diethyldithiocarbamate (I). To a solution of 1.00 g of tetraphenylantimony chloride in water, a solution of 0.42 g of sodium *N,N*-diethyldithiocarbamate in water was added. A colorless precipitate formed and was filtered off, dried, and crystallized from a toluene–heptane mixture

Table 2. Atomic coordinates, equivalent isotropic thermal parameters of non-hydrogen atoms $B = 4/3 \sum_{i=1}^{3} \sum_{j=1}^{3}(a_i a_j)B(i, j)$ ($Å^2$), and isotropic thermal parameters of hydrogen atoms in structure **I**

Atom	*x*	*y*	*z*	*B*	Atom	*x*	*y*	*z*	*B*
Sb^1	0.96060(3)	0.19505(5)	0.12359(1)	4.387(8)	C^{29}	0.9033(5)	0.4701(8)	0.0886(2)	7.6(2)
S^1	1.1058(1)	0.1246(2)	0.09558(6)	6.00(5)	H^7	0.953(3)	0.189(5)	0.036(1)	6(1)
S^2	1.0866(1)	0.2929(2)	0.16862(6)	5.66(5)	H^8	0.894(4)	0.088(7)	–0.016(2)	10(2)
N^1	1.2254(3)	0.2115(6)	0.1396(2)	5.9(1)	H^9	0.801(4)	–0.088(8)	–0.004(2)	11(2)
C^1	1.1468(4)	0.2100(7)	0.1354(2)	5.4(2)	H^{10}	0.773(3)	–0.148(5)	0.059(1)	5(1)
C^2	1.2783(4)	0.1484(8)	0.1094(2)	7.5(2)	H^{11}	0.825(3)	–0.028(5)	0.107(1)	4(1)
C^3	1.2953(5)	0.252(1)	0.0771(3)	11.4(3)	H^{13}	0.780(2)	0.186(4)	0.142(1)	1.8(9)
C^4	1.2654(4)	0.2792(8)	0.1726(2)	7.0(2)	H^{14}	0.678(3)	0.272(5)	0.182(1)	5(1)
C^5	1.2861(5)	0.1762(9)	0.2046(3)	9.1(3)	H^{15}	0.712(3)	0.444(6)	0.220(1)	7(2)
C^6	0.8973(4)	0.0909(7)	0.0764(2)	4.6(2)	H^{16}	0.843(3)	0.520(6)	0.229(2)	9(2)
C^7	0.9185(5)	0.1216(9)	0.0381(2)	7.3(2)	H^{17}	0.937(3)	0.416(6)	0.190(2)	8(2)
C^8	0.8808(5)	0.0548(9)	0.0072(2)	8.6(3)	H^{19}	0.956(2)	0.089(5)	0.211(1)	4(1)
C^9	0.8228(5)	–0.0395(9)	0.0143(2)	8.7(3)	H^{20}	0.964(2)	–0.107(5)	0.241(1)	4(1)
C^{10}	0.8012(5)	–0.0713(8)	0.0515(2)	7.1(2)	H^{21}	0.989(3)	–0.334(5)	0.217(1)	5(1)
C^{11}	0.8411(4)	–0.0090(8)	0.0826(2)	6.1(2)	H^{22}	1.010(3)	–0.331(5)	0.153(1)	7(2)
C^{12}	0.8692(3)	0.2813(7)	0.1613(2)	4.3(2)	H^{23}	0.998(3)	–0.131(6)	0.112(1)	6(1)
C^{13}	0.7919(4)	0.2403(8)	0.1598(2)	6.2(2)	H^{25}	1.085(3)	0.392(6)	0.074(1)	6(1)
C^{14}	0.7329(4)	0.3031(8)	0.1817(2)	6.4(2)	H^{26}	1.085(3)	0.562(6)	0.035(2)	8(2)
C^{15}	0.7540(4)	0.4063(8)	0.2078(2)	7.0(2)	H^{27}	0.961(4)	0.718(8)	0.032(2)	11(2)
C^{16}	0.8307(5)	0.4500(8)	0.2111(2)	7.0(2)	H^{28}	0.858(3)	0.642(6)	0.065(2)	9(2)
C^{17}	0.8874(4)	0.3875(8)	0.1879(2)	6.0(2)	H^{29}	0.851(5)	0.431(9)	0.100(2)	16(3)
C^{18}	0.9761(3)	0.0044(7)	0.1584(2)	4.7(2)	H^{31}	1.240(4)	0.275(7)	0.066(1)	9(2)
C^{19}	0.9653(4)	0.0064(8)	0.1985(2)	6.0(2)	H^{32}	1.323(3)	0.219(6)	0.062(2)	8(2)
C^{20}	0.9749(4)	–0.118(1)	0.2199(2)	7.6(2)	H^{33}	1.319(4)	0.331(6)	0.090(2)	11(2)
C^{21}	0.9916(5)	–0.2418(8)	0.2018(2)	6.9(2)	H^{41}	1.240(3)	0.348(6)	0.183(1)	7(2)
C^{22}	1.0009(4)	–0.2456(8)	0.1621(2)	6.6(2)	H^{42}	1.311(3)	0.326(5)	0.161(1)	7(2)
C^{23}	0.9925(4)	–0.1246(8)	0.1401(2)	5.5(2)	H^{51}	1.335(4)	0.098(8)	0.192(2)	12(2)
C^{24}	0.9704(4)	0.3942(8)	0.0906(2)	5.4(2)	H^{52}	1.234(3)	0.140(6)	0.213(1)	7(2)
C^{25}	1.0351(5)	0.4407(9)	0.0695(3)	8.6(2)	H^{53}	1.315(5)	0.204(8)	0.215(2)	15(3)
C^{26}	1.0291(5)	0.563(1)	0.0471(3)	10.3(3)	H^{211}	1.253(3)	0.065(5)	0.101(1)	4(1)
C^{27}	0.9618(6)	0.6377(9)	0.0455(2)	9.7(3)	H^{212}	1.325(4)	0.130(6)	0.126(1)	8(2)
C^{28}	0.8980(5)	0.5937(9)	0.0666(3)	9.7(3)					

to obtain 1.23 g (98%) of compound **I**, mp 148°C. IR spectrum, ν, cm^{-1}: 1430 s, 1305 w, 1272 v.s., 1212 s, 1180 s, 1142 s, 1065 v.s.

Reaction of sodium *N,N*-diethyldithiocarbamate with triphenylantimony chloride. A mixture of 1.12 g of triphenylantimony dichloride, 1.35 g of sodium *N,N*-diethyldithiocarbamate, and 10 ml of toluene was heated for 3 h at 100°C. The solvent was removed, and the residue was crystallized from hexane to obtain 0.65 g (83%) of yellow crystals, mp 62°C. The residue dissolved in hexane was chromatographed on a column with aluminum oxide. Elution with hexane gave 0.85 g (91%) of triphenylstibine, mp 48°C.

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