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Tetraphenyl- and Tetratolylantimony Complexes with *N*,*N*-Dialkyldithiocarbamate Ligands: Synthesis, X-Ray Diffraction Analysis, and ^{13}C and ^{15}N CP/MAS NMR Studies

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Abstract—Crystalline tetraphenylantimony and tetratolylantimony complexes with *N*,*N*-dialkyldithiocarbamate ligands $[Sb(C_6H_5)_4(S_2CNR_2)]$ (R = CH_3, C_2H_5, and C_3H_7 and $R_2 = (CH_2)_6$) were synthesized by ligand exchange reactions and studied by ^{13}C and ^{15}N CP/MAS NMR spectroscopy. X-ray diffraction analysis revealed that the complex $[Sb(n\text{-}CH_3\text{–}C_6H_4)_4\{S_2CN(C_3H_7)_2\}]$ exists as the single molecular form, while $[Sb(C_6H_5)_4\{S_2CN(CH_2)_6\}]$ exists as two molecular conformers. The ^{13}C and ^{15}N signals were assigned to the positions of the atoms in the isomeric structures $[Sb(C_6H_5)_4\{S_2CN(CH_2)_6\}]$ in terms of different degrees of double bonding in the formally single =N–C(S)S– bond.

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Organoantimony compounds are of interest as biocides, fungicides, components of catalysts, antioxidants, etc. [1]. That is why the synthesis of new organoantimony compounds and investigations of their structures and properties are important lines of modern coordination chemistry.

In this study, we obtained heteroligand complexes of tetraphenyl-$[Sb(C_6H_5)_4(S_2CNR_2)]$ (R = CH_3 (**I**), C_2H_5 (**II**), and C_3H_7 (**III**) and $R_2 = (CH_2)_6$ (**IV**)) and tetra(*p*-tolyl)antimony $[Sb(n\text{-}CH_3\text{–}C_6H_4)_4\{S_2CN(C_3H_7)_2\}]$ (**V**) and studied them by ^{13}C and ^{15}N CP/MAS NMR spectroscopy. Complexes **IV** and **V** were structurally characterized by X-ray diffraction data. Conformational isomerism was discovered in complex **IV**: its unit cell includes two molecular conformers of the complex. The ^{13}C and ^{15}N signals were assigned to the structural positions of the respective atoms of the dithiocarbamate groups in the resolved molecular isomers of complex **IV**.

EXPERIMENTAL

Complexes **I** and **II** were synthesized as described in [2, 3] and by ligand exchange reactions from pentaphenylantimony and bis(*N,N*-dialkyldithiocarbamato-*S,S*')triphenylantimony.

Synthesis of (*N*,*N*-dipropyldithiocarbamato-*S*,*S*')tetra(*p*-tolyl)antimony(V) (V). A solution of penta(*p*-tolyl)antimony (0.65 g) in benzene was added to a solution of bis(*N,N*-dipropyldithiocarbamato-*S,S*')tri(*p*-tolyl)antimony (0.50 g) in benzene. The reaction mixture was heated at 90°C for 1 h and cooled. The solvent was removed by evaporation and the residue was recrystallized from toluene–heptane (1 : 1). The yield of complex **V** was 0.90 g (78%), T_m = 151°C.

For $C_{35}H_{42}NS_2Sb$			
anal. calcd. (%):	63.44;	H, 6.34;	2.11.
Found (%):	63.06;	6.13;	2.03.

IR (ν, cm^{-1}): 1260 s, 1200 s, 1140 s, 1100 s, 1010 m, 910 m.

(*N*,*N*-Dipropyldithiocarbamato-*S*,*S*')tetraphenylantimony(V) (III) was obtained analogously. The yield of complex **III** was 83%, T_m = 141°C.

For $C_{31}H_{34}NS_2Sb$
anal. calcd. (%): 61.39; H, 5.61; N, 2.31.
Found (%): 61.27; H, 5.74; N, 2.22.

IR (ν, cm^{-1}): 1480 s, 1200 s, 1140 s, 1105 s, 1050 m, 1000 m.

(*N,N*-Cyclohexamethylenedithiocarbamato-*S,S'*)tetraphenylantimony(V) (IV) was synthesized by a reaction between aqueous solutions of tetraphenylantimony chloride and $Na\{S_2CN(CH_2)_6\} \cdot 2H_2O$ and recrystallized from benzene–heptane (1 : 1) as described in [2, 3]. The yield of complex **IV** was 57%, T_m = 153°C.

For $C_{31}H_{32}NS_2Sb$
anal. calcd. (%): 61.59; H, 5.30; N, 2.32.
Found (%): 61.44; H, 5.17; N, 2.14.

IR (ν, cm^{-1}): 1270 s, 1200 s, 1160 s, 1060 s, 970 s, 950 s, 880 s.

The starting sodium dialkyldithiocarbamates were characterized by ^{13}C and ^{15}N CP/MAS NMR spectroscopy:

$Na\{S_2CN(CH_3)_2\} \cdot xH_2O$ (Aldrich). ^{13}C NMR,

δ: 209.7 (51)*; 207.4 (43)* ($-S_2CN=$); 47.5 (39)*; 47.0 (31)* ($-CH_3$). ^{15}N NMR, δ: 116.7 ($=N-$).

$Na\{S_2CN(C_2H_5)_2\} \cdot 3H_2O$ (Fluka). ^{13}C NMR, δ: 206.5 (51)* ($-S_2CN=$); 48.6 (71)* ($=NCH_2-$); 13.2 ($-CH_3$). ^{15}N NMR, δ: 139.1 ($=N-$).

$Na\{S_2CN(C_3H_7)_2\} \cdot H_2O$. ^{13}C NMR, δ: 208.3 ($-S_2CN=$); 59.4, 57.9 (1 : 1) ($=NCH_2-$); 22.3, 21.5 (1 : 1) ($-CH_2-$); 12.6, 11.5 (1 : 1) ($-CH_3$).

$Na\{S_2CN(CH_2)_6\} \cdot 2H_2O$. ^{13}C NMR, δ: 206.3 ($-S_2CN=$); 60.3, 55.5 (1 : 1) ($=NCH_2-$); 29.8, 27.0, 26.2, 24.9 (1 : 1 : 1 : 1) ($-CH_2-$). ^{15}N NMR, δ: 135.2 ($=N-$).

IR spectra were recorded on a Hitachi-215 spectrometer (Nujol, NaCl plates).

^{13}C and ^{15}N MAS NMR spectra were recorded on CMX-360 (Varian/Chemagnetics Infinity-Plus) and CMX-400 pulse spectrometers (Chemagnetics Infinity) operating at 90.52 and 40.59 MHz (superconducting magnets with B_0 = 8.46 and 9.40 T, respectively; Fourier transform). The $^{13}C-^{1}H$ and $^{15}N-^{1}H$ cross polarization techniques were used; $^{13}C-^{1}H$ and $^{15}N-^{1}H$ dipolar interactions were suppressed by proton decoupling in a magnetic field with the corresponding proton resonance frequency [4].

In $^{13}C/^{15}N$ MAS NMR experiments, samples (~70/~350 mg) of the complexes were packed into ZrO_2 rotors 4.0/7.5 mm in diameter. The spinning rates were 8500 to 9800/3450 to 3760(1) Hz; the number of scans was 4620 to 10 000/2600 to 3700; the proton $\pi/2$pulse durations were 5.4/3.5 to 5.0 μs; the $^{1}H-^{13}C/^{1}H-^{15}N$ contact times were 1.5/1.5 to 2.5 ms; the pulses were spaced at 3.0 to 8.0/3.0 to 5.0 s. Isotropic ^{13}C and ^{15}N chemical shifts $\boldsymbol{\delta}$ (ppm) are referenced to a line of crystalline adamantane used as the external standard (δ = 38.56 ppm relative to tetramethylsilane [5]) and to crystalline NH_4Cl, respectively (δ = 0 ppm; –341 ppm on the absolute scale [6, 7]). The width of the reference line at δ = 38.56 ppm (2.4 Hz) for crystalline adamantane served as an indicator of the magnetic field uniformity.

The δ values were corrected for drift of the magnetic field strength during the measurements (its frequency equivalents for the $^{13}C/^{15}N$ nuclei were 0.098/0.033 Hz/h). The chemical shifts and the integrated intensity ratios for overlapping signals in the ^{13}C NMR spectra were additionally refined by fragment-by-fragment mathematical modeling with consideration of the line positions and widths and the contributions from the Lorentz and Gauss components to the line shapes.

X-ray diffraction analysis of complexes **IV** and **V** was performed on a Bruker SMART 1000 CCD diffractometer (prismatic single crystals; MoK_α radiation, λ = 0.71073 Å, graphite monochromator; crystal–detector distances 50 and 45 mm) at 296(2) and 173(1) K, respectively. Reflections were collected in sets composed of 906, 600, and 350 frames for φ = 0°, 90°, and 180°, respectively. In the ω scan mode, the scan step was 0.2° and the frame exposure time was 10 s. Absorption corrections were applied from the indices of the equivalent reflections. Structures **IV** and **V** were solved by the direct method and refined by the least-squares method in the full-matrix anisotropic approximation (on F^2) for non-hydrogen atoms. The hydrogen atoms were located geometrically and refined in the rider model. The collected data were edited and the unit cell parameters were refined with the SMART and SAINT-Plus programs [8]. Calculations for structure determination and refinement were performed with the SHELXTL/PC programs [9].

Selected crystallographic parameters of structures **IV** and **V** and a summary of data collection and refinement are given in Table 1. Atomic coordinates and thermal parameters are listed in Table 2. Bond lengths and angles are given in Table 3.

RESULTS AND DISCUSSION

In this study, we proposed a new method for the synthesis of tetraarylantimony *N,N*-dialkyldithiocarbamates by treating bis(*N,N*-dialkyldithiocarbamato-*S,S'*)triarylantimony with pentaarylantimony in a solution of an aromatic hydrocarbon:

$$Ar_5Sb + Ar_3Sb(S_2CNR_2)_2 \longrightarrow 2Ar_4SbS_2CNR_2,$$

$$Ar = Ph \text{ and } n\text{-}CH_3\text{–}C_6H_4;\ R = CH_3,\ C_2H_5, \text{ and } C_3H_7.$$

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*Refers to the asymmetric $^{13}C-^{14}N$ doublets, Hz.

Table 1. Selected crystallographic parameters and a summary of data collection and refinement for structures **IV** and **V**

Parameter	Value	
	IV	**V**
M	604.45	662.57
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pbca$
a, Å	18.804(3)	12.215(1)
b, Å	10.324(1)	19.102(2)
c, Å	29.614(4)	27.654(3)
β, deg	91.979(2)	90
V, Å^3	5746(1)	6452(1)
Z	8	8
ρ calcd, g/cm^3	1.397	1.364
μ, mm^{-1}	1.125	1.008
F(000)	2464	2736
Crystal shape (size, mm)	Prism (0.40 × 0.30 × 0.20)	Prism (0.32 × 0.17 × 0.10)
θ scan range, deg	3.80–28.01	3.55–26.02
Ranges of h, k, and l indices	$-24 \le h \le 23$, $-10 \le k \le 13$, $-37 \le l \le 39$	$-15 \le h \le 10$, $-20 \le k \le 23$, $-33 \le l \le 34$
Number of measured reflections	35552	34088
Number of independent reflections	13764 (R_{int} = 0.0381)	6338 (R_{int} = 0.060)
Number of reflections with $I > 2\sigma(I)$	10784	4699
Number of parameters refined	631	358
R factors ($F^2 > 2\sigma(F^2)$)	$R_1 = 0.0443$, $wR_2 = 0.0892$	$R_1 = 0.0482$, $wR_2 = 0.1037$
R factors for all reflections	$R_1 = 0.0623$, $wR_2 = 0.0957$	$R_1 = 0.0721$, $wR_2 = 0.1156$
GOOF	1.076	1.031
Residual electron density (min/max), e/Å^3	–0.944/0.764	–0.698/1.362

Note that antimony derivatives of the general formula Ar_4SbX (X is the monodentate organic or inorganic ligand) have been obtained analogously in [10].

The ^{13}C NMR spectra of crystalline antimony complexes **I–IV** (Fig. 1; Table 4) show resonance signals due to the =NC(S)S– groups and the alkyl substituents at the N atom in the dithiocarbamate ligands and signals due to the =CH– and =C= fragments in four aromatic rings C_6H_5–. The considerable broadening of the signals for the C atoms directly bound to the metal (δ 163–166 ppm) is due to interactions with “quadrupole” ^{121}Sb (I = 5/2, 57.25 at %) and ^{123}Sb nuclei (I = 7/2, 42.75 at %). A comparison of the ^{13}C and ^{15}N chemical shifts for the =NC(S)S– groups in antimony complexes and the corresponding sodium dithiocarbamates (Dtc) suggests that the covalent bonding of Dtc ligands increases the shielding of both carbon and nitrogen nuclei.

The signals for the =NC(S)S– fragment are structurally most informative. The ^{13}C NMR spectra of complexes **I–III** show singlets for this fragment (Figs. 1a–1c; Table 4), while the corresponding signal in the spectrum of complex **IV** appears as a 1 : 1 doublet (Fig. 1d). Therefore, complexes **I–III** exist in single molecular forms, while complex **IV** in the crystalline state is represented by two isomers. This correlates with the presence of a single signal in the ^{15}N NMR spectra of complexes **II** and **III** (Figs. 2a, 2b) and two signals of equal intensities in the spectrum of complex **IV** (Fig. 2c). To verify the existence of the isomeric forms, we carried out X-ray diffraction analysis of structure **IV**.

Table 2. Atomic coordinates ($\times 10^4$) and isotropic equivalent thermal parameters U_{equiv} for structures **IV** and **V**

Atom	x	y	z	U_{equiv}, Å^2	Atom	x	y	z	U_{equiv}, Å^2
IV									
Sb(1)	4692.8(1)	2715.2(2)	3685.53(7)	0.03986(7)	C(36)	6970(4)	6705(8)	4010(3)	0.159(4)
Sb(2)	9845.0(1)	4897.9(2)	3755.63(7)	0.03796(6)	C(37)	7226(4)	6457(8)	4507(3)	0.130(2)
S(1)	4245.0(5)	215.3(8)	3638.8(3)	0.0473(2)	C(38)	7837(3)	7270(6)	4681(2)	0.102(2)
S(2)	3665.0(5)	2099.6(9)	4283.5(3)	0.0528(2)	C(39)	10369(2)	5084(3)	3116(1)	0.0464(8)
S(3)	9321.5(6)	7351.4(8)	3728.8(3)	0.0551(2)	C(40)	10278(2)	4191(4)	2772(1)	0.068(1)
S(4)	9028.6(6)	5502.8(9)	4465.5(3)	0.0561(2)	C(41)	10595(3)	4354(5)	2365(1)	0.086(2)
N(1)	3020(2)	–90(3)	4045(1)	0.0526(7)	C(42)	11000(3)	5427(6)	2290(2)	0.079(1)
N(2)	8314(2)	7689(3)	4326(1)	0.0683(9)	C(43)	11088(2)	6339(5)	2624(2)	0.071(1)
C(1)	3586(2)	660(3)	3992(1)	0.0448(8)	C(44)	10783(2)	6153(4)	3032(1)	0.0567(9)
C(2)	2931(2)	–1356(4)	3822(2)	0.066(1)	C(45)	10035(2)	2954(3)	3997(1)	0.0418(7)
C(3)	2484(2)	–1299(5)	3386(2)	0.079(1)	C(46)	10219(2)	2758(3)	4449(1)	0.0537(9)
C(4)	1781(3)	–590(5)	3407(2)	0.087(1)	C(47)	10294(2)	1524(4)	4622(2)	0.071(1)
C(5)	1854(3)	850(5)	3479(2)	0.089(2)	C(48)	10200(2)	472(4)	4343(2)	0.077(1)
C(6)	1953(2)	1305(5)	3958(2)	0.085(2)	C(49)	10024(2)	645(4)	3895(2)	0.069(1)
C(7)	2389(2)	402(4)	4265(2)	0.072(1)	C(50)	9940(2)	1869(3)	3723(1)	0.0557(9)
C(8)	4768(2)	4699(3)	3909(1)	0.0532(9)	C(51)	8815(2)	4421(3)	3441(1)	0.0491(8)
C(9)	4643(4)	4976(4)	4355(2)	0.103(2)	C(52)	8391(2)	3493(4)	3624(2)	0.065(1)
C(10)	4668(4)	6237(5)	4510(2)	0.129(3)	C(53)	7739(2)	3169(6)	3418(2)	0.093(2)
C(11)	4832(3)	7216(4)	4231(2)	0.098(2)	C(54)	7513(3)	3803(7)	3035(2)	0.101(2)
C(12)	4959(3)	6965(4)	3796(2)	0.079(1)	C(55)	7929(3)	4729(6)	2847(2)	0.090(2)
C(13)	4920(2)	5707(4)	3624(2)	0.065(1)	C(56)	8581(2)	5039(4)	3048(1)	0.065(1)
C(14)	5393(2)	2445(3)	3129(1)	0.0459(8)	C(57)	10776(2)	5630(3)	4139(1)	0.0427(7)
C(15)	5378(2)	3239(4)	2749(1)	0.0586(9)	C(58)	11404(2)	4983(4)	4068(1)	0.0531(9)
C(16)	5782(3)	2935(5)	2382(1)	0.077(1)	C(59)	12027(2)	5309(4)	4304(1)	0.067(1)
C(17)	6174(3)	1841(5)	2378(2)	0.080(1)	C(60)	12016(3)	6302(5)	4616(1)	0.072(1)
C(18)	6191(2)	1036(5)	2746(2)	0.074(1)	C(61)	11406(3)	6956(4)	4687(1)	0.072(1)
C(19)	5815(2)	1344(4)	3123(1)	0.0571(9)	C(62)	10779(2)	6630(3)	4450(1)	0.0563(9)
C(20)	3768(2)	3035(3)	3236(1)	0.0488(8)	**V**				
C(21)	3688(2)	2341(4)	2833(1)	0.061(1)	Sb	7953.7(2)	2438.9(1)	3507.74(7)	0.02823(5)
C(22)	3098(3)	2558(5)	2547(2)	0.079(1)	S(1)	9556.2(7)	3343.2(5)	3924.9(3)	0.0382(2)
C(23)	2595(3)	3428(6)	2658(2)	0.094(2)	S(2)	8493.6(7)	2173.7(4)	4448.1(3)	0.0334(2)
C(24)	2664(2)	4118(5)	3048(2)	0.088(2)	N	9389(2)	3263(1)	4888(1)	0.0310(6)
C(25)	3252(2)	3934(4)	3340(2)	0.063(1)	C(1)	9174(2)	2960(2)	4465(1)	0.0296(7)
C(26)	5507(2)	2074(3)	4183(1)	0.0434(7)	C(2)	9055(3)	2948(2)	5353(1)	0.0410(9)
C(27)	5450(2)	1059(3)	4479(1)	0.0535(9)	C(3)	7864(4)	3075(2)	5481(2)	0.068(1)
C(28)	6018(2)	728(4)	4766(1)	0.066(1)	C(4)	7473(4)	3792(2)	5449(2)	0.077(2)
C(29)	6644(3)	1407(5)	4753(2)	0.075(1)	C(5)	10054(3)	3905(2)	4916(1)	0.0395(9)
C(30)	6708(3)	2420(5)	4457(2)	0.078(1)	C(6)	11260(3)	3741(2)	4967(1)	0.045(1)
C(31)	6139(2)	2759(4)	4175(1)	0.061(1)	C(7)	11971(3)	4394(2)	4972(2)	0.058(1)
C(32)	8837(2)	6923(3)	4187(1)	0.0508(8)	C(11)	6953(3)	3292(2)	3787(1)	0.0325(8)
C(33)	8117(3)	8890(5)	4090(2)	0.094(2)	C(12)	6898(3)	3912(2)	3526(1)	0.0359(8)
C(34)	7557(4)	8711(7)	3720(2)	0.123(2)	C(13)	6248(3)	4456(2)	3691(1)	0.0394(9)
C(35)	6899(4)	8015(8)	3845(3)	0.138(3)	C(14)	5647(3)	4409(2)	4113(1)	0.0390(9)

Table 2. (Contd.)

Atom	x	y	z	U_{equiv}, Å^2	Atom	x	y	z	U_{equiv}, Å^2
C(15)	5693(3)	3778(2)	4364(1)	0.0397(9)	C(33)	8926(3)	3364(2)	2112(1)	0.0370(8)
C(16)	6331(3)	3226(2)	4203(1)	0.0392(9)	C(34)	8015(3)	3339(2)	1816(1)	0.0360(8)
C(17)	4954(3)	5012(2)	4284(2)	0.054(1)	C(35)	7072(3)	3042(2)	2001(1)	0.0444(9)
C(21)	9249(2)	1715(2)	3310(1)	0.0293(7)	C(36)	7034(3)	2788(2)	2475(1)	0.0404(9)
C(22)	10294(3)	1676(2)	3508(1)	0.0363(8)	C(37)	8038(3)	3623(2)	1308(1)	0.051(1)
C(23)	11062(3)	1224(2)	3316(1)	0.0414(9)	C(41)	6676(2)	1668(1)	3534(1)	0.0261(7)
C(24)	10812(3)	790(2)	2933(1)	0.0374(9)	C(42)	6901(2)	988(2)	3682(1)	0.0292(7)
C(25)	9759(3)	815(2)	2744(1)	0.0375(9)	C(43)	6095(3)	485(2)	3704(1)	0.0328(8)
C(26)	8997(3)	1283(2)	2926(1)	0.0338(8)	C(44)	5022(3)	642(2)	3578(1)	0.0295(7)
C(27)	11643(3)	288(2)	2716(1)	0.053(1)	C(45)	4779(2)	1325(2)	3436(1)	0.0286(7)
C(31)	7940(2)	2827(2)	2773(1)	0.0306(7)	C(46)	5593(3)	1835(2)	3417(1)	0.0302(8)
C(32)	8888(3)	3115(2)	2580(1)	0.0367(8)	C(47)	4153(3)	76(2)	3575(1)	0.0412(9)

Structure **IV** is made up of two crystallographically independent molecules $[Sb(C_6H_5)_4\{S_2CN(CH_2)_6\}]$ (Fig. 3; Table 3). In either molecule, the antimony atom is in the distorted octahedral environment $[C_4S_2]$. In the equatorial plane, the Sb atom coordinates the Dtc ligand through two S atoms and two most firmly bound phenyl fragments. Two other, looser phenyl fragments are in the axial positions. The axial angles CSbC appreciably deviate from 180° in both molecules (169.0° and 169.6°).

The bidentate coordination of the Dtc ligands gives rise to four-membered chelate rings SbS_2C. Although chelate rings of this type are usually planar, the torsion angles in the fragment SbS_2C of structure **IV** indicate its substantial nonplanarity. The dihedral angles between the SbSC planes are 164.0° (Sb(1) in molecule A) and –168.3° (Sb(2) in molecule B). The dihedral angles between the SbS_2 and CS_2 planes are 160.9° (A) and –166.1° (B). Thus, the four-membered chelate rings are folded along both the diagonals S–S and Sb–C. The distance between the opposite S atoms (S···S 2.960 and 2.965 Å) are appreciably shorter than the Sb···C distance (3.129 and 3.131 Å). In the six-membered C_6H_5 rings, the C–C bond lengths range from 1.34 to 1.396 Å and the CCC angles are close to 120°, which is characteristic of the sp^2-hybridized orbitals of the C atom (117.2°–121.9°).

In dithiocarbamate ligands, the N–C(S)S bond is substantially shorter than the N–CH_2 bond, which suggests a partially double character of the formally single bond in the former case (“contamination” of the sp^2-hybridized state of the N atom with the sp^3-one). However, one of the carbon atoms (C(7) and C(38)) in both $C_2NC(S)S$ fragments deviates from its plane.

A comparative analysis of the X-ray diffraction and NMR data revealed a structural similarity of molecules A and B and, nevertheless, allowed them to be classified as conformational isomers (when a polyatomic molecular system reaches equilibrium in two or more energy-close configurations). The most substantial differences between the conformers under discussion are in the dithiocarbamate ligands. In molecule A, the Dtc ligand is coordinated in the anisobidentate manner since one Sb–S bond (2.717 Å) is stronger than the other (2.741 Å) to within the error of determination. In contrast, this ligand in molecule B is virtually isobidentate (Sb–S 2.721 and 2.724 Å) and the bonds are generally stronger (Table 3). The strengths of the corresponding carbon–carbon bonds (C(3)–C(4) and C(36)–C(37), C(4)–C(5) and C(35)–C(36)) in the cyclic fragments $N(CH_2)_6$ of molecules A and B somewhat differ as well (Table 3). The seven-membered ring in molecule B is also more distorted because of the larger scatter of the C–C bond lengths (1.442–1.553 Å) as compared to that in molecule A (1.501–1.522 Å).

Structure **V** consists of a single independent molecule $[Sb(n\text{-}CH_3\text{–}C_6H_4)_4\{S_2CN(C_3H_7)_2\}]$ (Fig. 4; Table 3). The molecular structures of complexes **V** and **IV** are similar. The polyhedron $[SbC_4S_2]$ of the antimony atom is a distorted octahedron. Its equatorial

Table 3. Bond lengths *d*, bond angles ω, and torsion angles φ in complexes **IV** and **V**

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
IV							
Molecule A		Molecule B		Molecule A		MoleculeB	
Sb(1)–C(8)	2.156(3)	Sb(2)–C(39)	2.169(3)	C(11)–C(12)	1.346(7)	C(41)–C(42)	1.366(7)
Sb(1)–C(14)	2.162(4)	Sb(2)–C(45)	2.155(3)	C(12)–C(13)	1.396(5)	C(40)–C(41)	1.374(6)
Sb(1)–C(20)	2.179(3)	Sb(2)–C(51)	2.185(3)	C(14)–C(19)	1.387(5)	C(45)–C(46)	1.386(5)
Sb(1)–C(26)	2.188(3)	Sb(2)–C(57)	2.180(3)	C(14)–C(15)	1.393(5)	C(45)–C(50)	1.392(4)
Sb(1)–S(1)	2.7169(9)	Sb(2)–S(4)	2.7238(10)	C(15)–C(16)	1.382(6)	C(49)–C(50)	1.369(5)
Sb(1)–S(2)	2.741(1)	Sb(2)–S(3)	2.7211(10)	C(16)–C(17)	1.349(7)	C(48)–C(49)	1.370(6)
S(1)–C(1)	1.711(4)	S(4)–C(32)	1.714(4)	C(17)–C(18)	1.368(6)	C(47)–C(48)	1.372(6)
S(2)–C(1)	1.723(3)	S(3)–C(32)	1.719(4)	C(18)–C(19)	1.381(5)	C(46)–C(47)	1.378(5)
N(1)–C(1)	1.330(4)	N(2)–C(32)	1.338(5)	C(20)–C(25)	1.386(5)	C(51)–C(56)	1.387(5)
N(1)–C(2)	1.471(5)	N(2)–C(38)	1.471(6)	C(20)–C(21)	1.395(5)	C(51)–C(52)	1.369(5)
N(1)–C(7)	1.464(5)	N(2)–C(33)	1.464(6)	C(21)–C(22)	1.389(6)	C(52)–C(53)	1.392(6)
C(2)–C(3)	1.516(6)	C(37)–C(38)	1.500(8)	C(22)–C(23)	1.354(7)	C(53)–C(54)	1.363(8)
C(3)–C(4)	1.514(6)	C(36)–C(37)	1.553(10)	C(23)–C(24)	1.361(7)	C(54)–C(55)	1.365(8)
C(4)–C(5)	1.507(7)	C(35)–C(36)	1.442(9)	C(24)–C(25)	1.392(6)	C(55)–C(56)	1.382(6)
C(5)–C(6)	1.501(7)	C(34)–C(35)	1.489(9)	C(26)–C(31)	1.385(5)	C(57)–C(58)	1.380(5)
C(6)–C(7)	1.522(7)	C(33)–C(34)	1.505(7)	C(26)–C(27)	1.374(5)	C(57)–C(62)	1.384(4)
C(8)–C(13)	1.376(5)	C(39)–C(40)	1.382(5)	C(27)–C(28)	1.385(5)	C(61)–C(62)	1.391(5)
C(8)–C(9)	1.378(6)	C(39)–C(44)	1.378(5)	C(28)–C(29)	1.370(6)	C(60)–C(61)	1.355(6)
C(9)–C(10)	1.381(6)	C(43)–C(44)	1.369(5)	C(29)–C(30)	1.372(6)	C(59)–C(60)	1.381(6)
C(10)–C(11)	1.348(8)	C(42)–C(43)	1.370(7)	C(30)–C(31)	1.381(5)	C(58)–C(59)	1.384(5)
Angle	ω, deg	Angle	ω,deg	Angle	ω, deg	Angle	ω, deg
C(8)Sb(1)C(14)	108.7(1)	C(45)Sb(2)C(39)	107.5(1)	C(1)N(1)C(2)	122.9(3)	C(32)N(2)C(38)	121.2(4)
C(8)Sb(1)C(20)	95.0(1)	C(39)Sb(2)C(51)	94.0(1)	C(7)N(1)C(2)	115.3(3)	C(33)N(2)C(38)	116.0(4)
C(14)Sb(1)C(20)	92.8(1)	C(45)Sb(2)C(51)	93.6(1)	N(1)C(1)S(1)	121.0(3)	N(2)C(32)S(4)	120.2(3)
C(8)Sb(1)C(26)	92.5(1)	C(39)Sb(2)C(57)	92.7(1)	N(1)C(1)S(2)	119.9(3)	N(2)C(32)S(3)	120.3(3)
C(14)Sb(1)C(26)	92.5(1)	C(45)Sb(2)C(57)	91.9(1)	S(1)C(1)S(2)	119.1(2)	S(4)C(32)S(3)	119.5(2)
C(20)Sb(1)C(26)	169.0(1)	C(57)Sb(2)C(51)	169.6(1)	N(1)C(2)C(3)	113.5(3)	N(2)C(38)C(37)	113.4(5)
C(8)Sb(1)S(1)	159.3(1)	C(39)Sb(2)S(4)	159.70(9)	C(4)C(3)C(2)	116.3(4)	C(38)C(37)C(36)	116.2(6)
C(14)Sb(1)S(1)	91.98(9)	C(45)Sb(2)S(4)	92.65(9)	C(5)C(4)C(3)	114.1(4)	C(35)C(36)C(37)	119.8(7)
C(20)Sb(1)S(1)	82.73(9)	C(51)Sb(2)S(4)	82.0(1)	C(6)C(5)C(4)	116.8(4)	C(36)C(35)C(34)	118.0(6)
C(26)Sb(1)S(1)	87.44(9)	C(57)Sb(2)S(4)	89.02(9)	C(5)C(6)C(7)	114.8(4)	C(35)C(34)C(33)	116.3(6)
C(8)Sb(1)S(2)	93.6(1)	C(39)Sb(2)S(3)	93.83(9)	N(1)C(7)C(6)	112.0(4)	N(2)C(33)C(34)	113.7(4)
C(14)Sb(1)S(2)	157.51(9)	C(45)Sb(2)S(3)	158.61(9)	C(13)C(8)C(9)	118.5(4)	C(44)C(39)C(40)	117.2(4)
C(20)Sb(1)S(2)	82.2(1)	C(51)Sb(2)S(3)	83.00(9)	C(13)C(8)Sb(1)	122.9(3)	C(40)C(39)Sb(2)	122.5(3)
C(26)Sb(1)S(2)	89.29(9)	C(57)Sb(2)S(3)	88.66(9)	C(9)C(8)Sb(1)	118.6(3)	C(44)C(39)Sb(2)	120.2(3)
S(1)Sb(1)S(2)	65.69(3)	S(3)Sb(2)S(4)	65.98(3)	C(8)C(9)C(10)	120.6(5)	C(43)C(44)C(39)	121.9(4)
C(1)S(1)Sb(1)	86.8(1)	C(32)S(4)Sb(2)	86.6(1)	C(11)C(10)C(9)	120.6(5)	C(44)C(43)C(42)	119.7(4)
C(1)S(2)Sb(1)	85.8(1)	C(32)S(3)Sb(2)	86.6(1)	C(12)C(11)C(10)	119.6(4)	C(41)C(42)C(43)	119.8(4)
C(1)N(1)C(7)	121.0(3)	C(32)N(2)C(33)	122.2(4)	C(11)C(12)C(13)	121.3(5)	C(42)C(41)C(40)	120.1(4)
C(1)N(1)C(2)	122.9(3)	C(32)N(2)C(38)	121.2(4)	C(8)C(13)C(12)	119.3(4)	C(41)C(40)C(39)	121.4(4)
C(7)N(1)C(2)	115.3(3)	C(33)N(2)C(38)	116.0(4)	C(19)C(14)C(15)	117.9(4)	C(46)C(45)C(50)	118.0(3)
N(1)C(1)S(1)	121.0(3)	N(2)C(32)S(4)	120.2(3)	C(19)C(14)Sb(1)	118.6(3)	C(46)C(45)Sb(2)	119.3(2)

Table 3. (Contd.)

Angle	ω, deg	Angle	ω, deg
C(15)C(14)Sb(1)	123.0(3)	C(50)C(45)Sb(2)	122.6(3)
C(16)C(15)C(14)	120.4(4)	C(49)C(50)C(45)	120.9(4)
C(17)C(16)C(15)	120.7(4)	C(50)C(49)C(48)	120.1(4)
C(16)C(17)C(18)	120.0(4)	C(49)C(48)C(47)	120.2(4)
C(17)C(18)C(19)	120.3(4)	C(48)C(47)C(46)	119.9(4)
C(18)C(19)C(14)	120.5(4)	C(47)C(46)C(45)	120.9(4)
C(25)C(20)C(21)	118.6(3)	C(52)C(51)C(56)	118.8(4)
C(25)C(20)Sb(1)	121.0(3)	C(56)C(51)Sb(2)	120.5(3)
C(21)C(20)Sb(1)	120.3(3)	C(52)C(51)Sb(2)	120.7(3)
C(22)C(21)C(20)	119.9(4)	C(51)C(52)C(53)	120.7(5)
C(23)C(22)C(21)	120.6(5)	C(54)C(53)C(52)	119.5(5)
C(22)C(23)C(24)	120.4(4)	C(53)C(54)C(55)	120.6(5)
C(23)C(24)C(25)	120.5(5)	C(54)C(55)C(56)	119.9(5)
C(20)C(25)C(24)	119.9(5)	C(55)C(56)C(51)	120.4(5)
C(27)C(26)C(31)	119.1(3)	C(58)C(57)C(62)	118.6(3)
C(27)C(26)Sb(1)	126.3(3)	C(62)C(57)Sb(2)	126.2(3)
C(31)C(26)Sb(1)	114.5(2)	C(58)C(57)Sb(2)	115.2(2)
C(26)C(27)C(28)	120.3(4)	C(57)C(62)C(61)	120.0(4)
C(29)C(28)C(27)	120.1(4)	C(60)C(61)C(62)	120.6(4)
C(28)C(29)C(30)	120.2(4)	C(61)C(60)C(59)	120.4(4)
C(29)C(30)C(31)	119.8(4)	C(60)C(59)C(58)	119.1(4)
C(30)C(31)C(26)	120.6(4)	C(57)C(58)C(59)	121.3(4)

Angle	φ, deg	Angle	φ, deg
C(2)N(1)C(1)S(1)	2.2(5)	C(33)N(2)C(32)S(3)	1.8(5)
C(2)N(1)C(1)S(2)	−177.4(3)	C(33)N(2)C(32)S(4)	−178.0(3)
C(7)N(1)C(1)S(1)	−166.6(3)	C(38)N(2)C(32)S(3)	172.5(1)
C(7)N(1)C(1)S(2)	13.8(5)	C(38)N(2)C(32)S(4)	−7.4(5)
Sb(1)S(1)C(1)N(1)	164.4(3)	Sb(2)S(3)C(32)N(2)	−168.2(3)
Sb(1)S(2)C(1)N(1)	−164.6(3)	Sb(2)S(4)C(32)N(2)	168.2(3)
S(1)Sb(1)C(1)S(2)	164.0(3)	S(3)Sb(2)C(32)S(4)	−168.3(3)
Sb(1)S(1)S(2)C(1)	160.9(3)	Sb(2)S(3)S(4)C(32)	−166.1(3)

V

Bond	d, A	Bond	d, A
Sb–C(11)	2.179(3)	C(21)–C(22)	1.391(4)
Sb–C(21)	2.171(3)	C(21)–C(26)	1.380(4)
Sb–C(31)	2.162(3)	C(22)–C(23)	1.381(5)
Sb–C(41)	2.147(3)	C(23)–C(24)	1.381(5)
Sb–S(1)	2.8542(9)	C(24)–C(25)	1.389(5)
Sb–S(2)	2.7303(8)	C(24)–C(27)	1.519(5)
S(1)–C(1)	1.727(3)	C(25)–C(26)	1.384(5)
S(2)–C(1)	1.717(3)	C(31)–C(32)	1.389(4)
N–C(1)	1.331(4)	C(31)–C(36)	1.383(4)
N–C(2)	1.479(4)	C(32)–C(33)	1.379(5)
N–C(5)	1.472(4)	C(33)–C(34)	1.382(5)
C(2)–C(3)	1.517(6)	C(34)–C(35)	1.384(5)
C(3)–C(4)	1.452(6)	C(34)–C(37)	1.507(5)
C(5)–C(6)	1.512(5)	C(35)–C(36)	1.396(5)

Bond	d, A	Bond	d, A
C(6)–C(7)	1.521(5)	C(41)–C(42)	1.389(4)
C(11)–C(12)	1.387(4)	C(41)–C(46)	1.399(4)
C(11)–C(16)	1.383(5)	C(42)–C(43)	1.377(4)
C(12)–C(13)	1.384(5)	C(43)–C(44)	1.390(4)
C(13)–C(14)	1.383(5)	C(44)–C(45)	1.394(4)
C(14)–C(15)	1.392(5)	C(44)–C(47)	1.515(4)
C(14)–C(17)	1.506(5)	C(45)–C(46)	1.392(4)
C(15)–C(16)	1.385(5)		

Angle	ω, deg	Angle	ω, deg
C(21)SbC(11)	167.0(1)	C(15)C(14)C(17)	121.9(3)
C(31)SbC(11)	94.2(1)	C(16)C(11)C(12)	118.9(3)
C(31)SbC(21)	89.3(1)	C(16)C(15)C(14)	121.4(3)
C(41)SbC(11)	95.4(1)	C(22)C(21)Sb	127.1(2)
C(41)SbC(21)	95.8(1)	C(26)C(21)Sb	114.3(2)
C(41)SbC(31)	105.1(1)	C(21)C(26)C(25)	121.0(3)
C(11)SbS(1)	77.82(8)	C(22)C(23)C(24)	121.4(3)
C(21)SbS(1)	89.28(8)	C(23)C(22)C(21)	120.4(3)
C(31)SbS(1)	100.23(8)	C(23)C(24)C(25)	118.2(3)
C(41)SbS(1)	154.16(8)	C(23)C(24)C(27)	122.3(3)
C(11)SbS(2)	86.37(8)	C(25)C(24)C(27)	119.6(3)
C(21)SbS(2)	86.89(8)	C(26)C(21)C(22)	118.4(3)
C(31)SbS(2)	163.79(8)	C(26)C(25)C(24)	120.6(3)
C(41)SbS(2)	90.93(8)	C(32)C(31)Sb	119.4(2)
S(2)SbS(1)	64.00(2)	C(36)C(31)Sb	123.3(2)
C(1)S(1)Sb	84.7(1)	C(31)C(36)C(35)	121.0(3)
C(1)S(2)Sb	88.9(1)	C(32)C(33)C(34)	121.1(3)
C(1)NC(2)	122.2(3)	C(33)C(32)C(31)	121.8(3)
C(1)NC(5)	121.2(3)	C(33)C(34)C(35)	117.7(3)
C(5)NC(2)	116.5(3)	C(33)C(34)C(37)	121.7(3)
NC(1)S(1)	121.4(2)	C(34)C(35)C(36)	121.2(3)
NC(1)S(2)	120.0(2)	C(35)C(34)C(37)	120.6(3)
S(2)C(1)S(1)	118.6(2)	C(36)C(31)C(32)	117.2(3)
NC(2)C(3)	113.7(3)	C(42)C(41)Sb	120.5(2)
C(4)C(3)C(2)	116.9(4)	C(46)C(41)Sb	121.5(2)
NC(5)C(6)	111.7(3)	C(42)C(41)C(46)	117.9(3)
C(5)C(6)C(7)	112.8(3)	C(42)C(43)C(44)	120.8(3)
C(12)C(11)Sb	118.8(2)	C(43)C(42)C(41)	121.6(3)
C(16)C(11)Sb	122.3(2)	C(43)C(44)C(45)	118.3(3)
C(11)C(16)C(15)	120.5(3)	C(43)C(44)C(47)	120.5(3)
C(13)C(12)C(11)	119.9(3)	C(45)C(44)C(47)	121.2(3)
C(13)C(14)C(15)	117.1(3)	C(45)C(46)C(41)	120.4(3)
C(13)C(14)C(17)	120.9(3)	C(46)C(45)C(44)	120.9(3)
C(14)C(13)C(12)	122.2(3)		

Angle	φ, deg	Angle	φ, deg
S(1)C(1)NC(2)	179.1(2)	S(2)C(1)NC(5)	174.6(2)
S(1)C(1)NC(5)	−5.8(4)	S(2)SbC(1)S(1)	160.7(2)
S(2)C(1)NC(2)	−0.5(4)	SbS(2)S(1)C(1)	157.2(2)

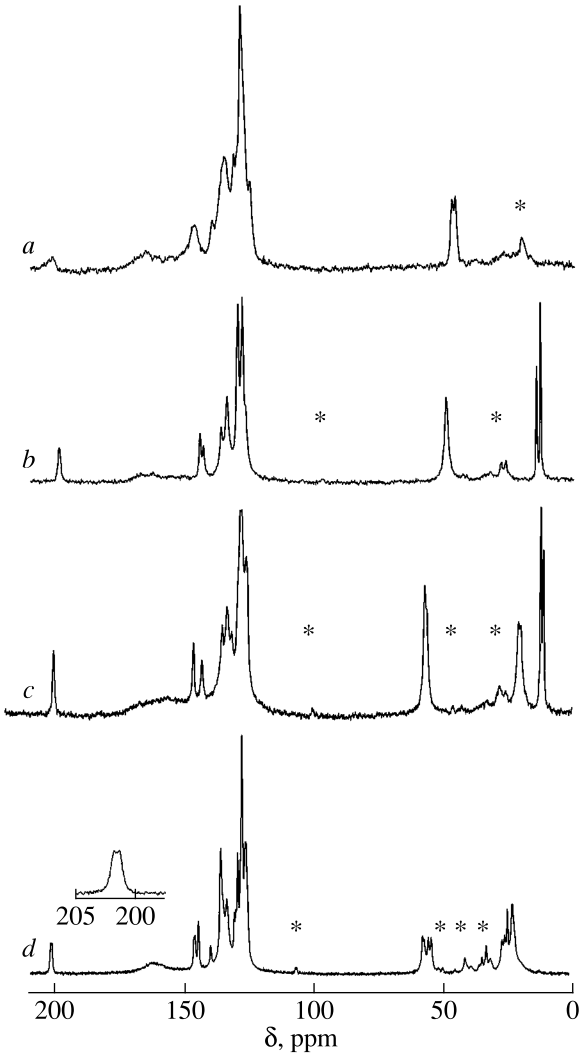

Fig. 1. ^{13}C MAS NMR spectra of polycrystalline complexes **I**–**IV** of the general formula $[Sb(C_6H_5)_4(S_2CNR_2)]$: R = (*a*) CH_3 , (*b*) C_2H_5, and (*c*) C_3H_7; (*d*) $R_2 = (CH_2)_6$. The numbers of scans/spinning rates (Hz) are (*a*) 4560/5500, (*b*) 10 000/9200, (*c*) 7700/9100, and (*d*) 10 000/8500. Sidebands due to the spinning are asterisked.

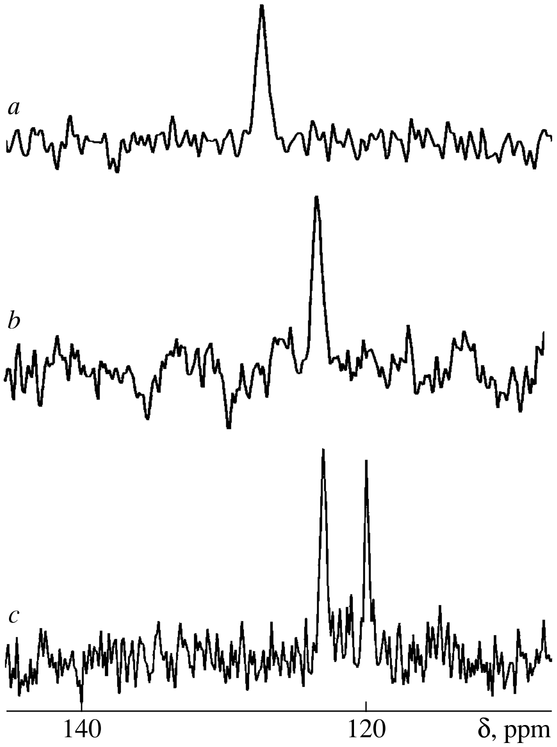

Fig. 2. ^{15}N MAS NMR spectra of polycrystalline complexes **II**–**IV** of the general formula $[Sb(C_6H_5)_4(S_2CNR_2)]$: R = (*a*) C_2H_5 and (*b*) C_3H_7; (*c*) $R_2 = (CH_2)_6$. The numbers of scans/spinning rates (Hz) are (*a*) 3052/3450, (*b*) 2600/3760, and (*c*) 3700/3760.

plane is made up of the bidentate *N,N*-dipropyldithiocarbamate ligand and two most firmly bound monodentate *p*-tolyl ligands. The looser tolyl ligands are in the axial positions. The axial CSbC angle in the octahedron is 167.0°, appreciably deviating from ideal 180°. The dipropyldithiocarbamate ligand is coordinated in the anisobidentate manner since one Sb–S bond (2.7303 Å) is substantially shorter than the other (2.8542 Å). The coordination of the dithiocarbamate ligand gives rise to a four-membered chelate ring SbS_2C.

The torsion angles in this ring suggest its nonplanar geometry (Table 3). This is confirmed by the dihedral angles between two SbSC planes (160.7°) and between the SbSS and SSC planes (157.3°). As with complex **IV**, the four-membered chelate ring in complex **V** is folded along the Sb–C and S–S diagonals. The S···S distance (2.961 Å) is shorter than the Sb···C one (3.129 Å). In the six-membered rings p-CH_3–C_6H_4, the C–C bonds (1.377–1.399 Å) are on average somewhat longer than in phenyl rings. The CCC angles are not strictly equal to 120° (117.1°–122.3°). The fragment C_2N–C(S)S (Table 3) is virtually planar (the C(5) atom slightly deviates from the plane) and the N–C(S)S bond is short.

Assignment of ^{13}C and ^{15}N NMR signals to the atoms in the isomeric molecular forms of complex **IV** was based on different degrees of double bonding in the fragments =N–C(S)S– [11–14]. The partial double bond character causes the electron density transfer from the N atom toward the –C(S)S– group; as the result, the electron shielding of the N nucleus diminishes, while that of the C atom increases. The N(1)–C(1) bond in molecule A (1.330 Å) is slightly stronger than in molecule B (N(2)–C(32) 1.338 Å). Therefore, the bond order in molecule A is higher and the electron density shift $=N \longrightarrow C(S)S$– is more considerable. Thus, the ^{15}N NMR signal at δ 123.0 ppm should be assigned to the less shielded N(1) atom, while the signal at δ 120.0 ppm, to the N(2) atom. Analogously, the ^{13}C NMR signals at δ 201.4 and 201.9 ppm

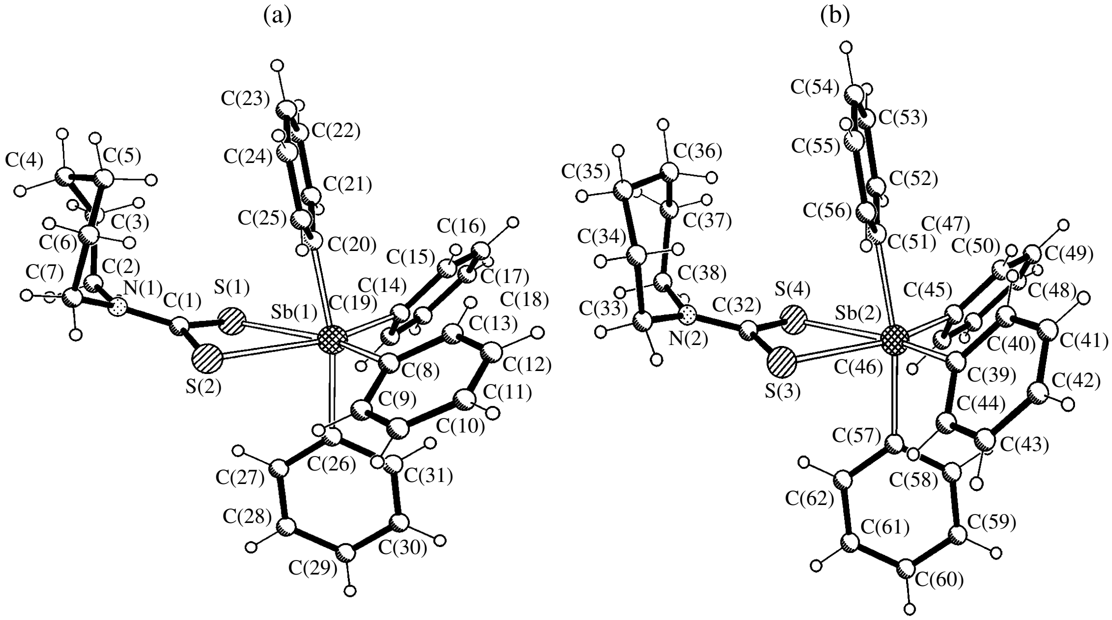

Fig. 3. Structures of two molecules (a) A and (b) B in complex **IV**.

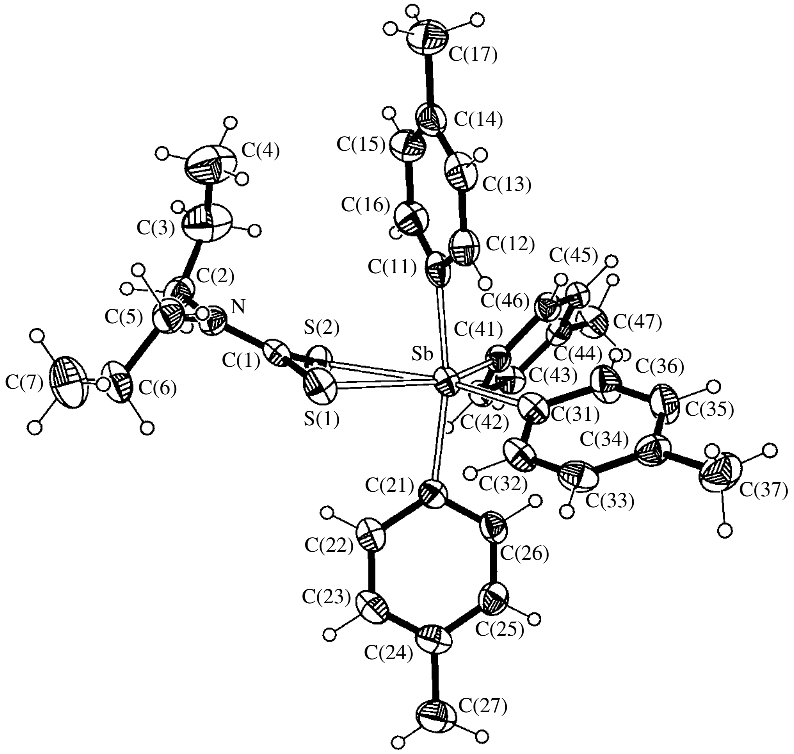

Fig. 4. Structure **V** with atomic thermal displacement ellipsoids (50% probability).

Table 4. ^{13}C and ^{15}N chemical shifts δ (ppm) for complexes **I–IV** with reference to TMS and $\mathrm{N_H4Cl}$, respectively

Complex	δ^{13}C					δ^{15}N
	$-S_2CN=$	$=NCH_2-$	$-CH_2-$	$-CH_3-$	C_6H_5-	$-N=$
$[Sb(C_6H_5)_4\{S_2CN(CH_3)_2\}]$ (**I**)	201.7			47.3, 46.1 (1 : 1)	166, 147.1, 139.9, 135.3, 131.4, 128.8, 125.3	
$[Sb(C_6H_5)_4\{S_2CN(C_2H_5)_2\}]$ (**II**)	198.9	49.3		14.4, 12.8 (1 : 1)	163, 144.5, 143.2, 136.4, 134.0, 130.2, 129.8, 128.47, 128.1, 126.9	127.3
$[Sb(C_6H_5)_4\{S_2CN(C_3H_7)_2\}]$ (**III**)	201.2	57.4, 56.7 (1 : 1)	20.9, 20.1 (1 : 1)	12.2, 11.3 (1 : 1)	*, 147.1, 143.8, 135.9, 134.0, 132.2, 129.8, 129.0, 128.3, 126.6	123.3
$[Sb(C_6H_5)_4\{S_2CN(CH_2)_6\}]$ (**IV**)	201.9, 201.4 (1 : 1)	59.1, 58.5, 56.8, 55.7 (1 : 1 : 1 : 1)	28.4, 27.4, 26.4, 24.5, 23.9 (1 : 1 : 2 : 2 : 2)		163, 146.9, 146.6, 145.2, 140.5, 136.6, 135.8, 134.3, 131.3, 130.7, 130.0, 129.0, 128.4, 127.2, 126.8, 126.2	123.0, 120.0 (1 : 1)

* The chemical shift was not determined because of broadening of the ^{13}C NMR signal for the ≡C–Sb group.

were assigned to the more and less shielded carbon nuclei (C(1) and C(32), respectively).

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