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Syntheses and Properties of Some Trimethylantimony(V) Complexes of Dithiocarbonate Derivatives

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New stable trimethylantimony(V) complexes of some dithiocarbonate derivatives, $(CH_3)_3SbL_2$, where HL= secondary amine-*N*-carbodithioic acid or *O*-alkyl dithiocarbonic acid, have been synthesized by the metathetical reaction between dibromotrimethylantimony(V) and the alkali salts of ligands. In these compounds, the antimony is kept quinquevalent. The ^{1}H-NMR peak of the methyl protons of all of these compounds appears as a singlet even at −60 °C. Therefore, the most probable structure for these compounds is the trigonal bipyramidal one, where two unidentate dithiocarbonate derivative ligands bond to antimony from the apical directions.

The R_3SbL_2 type quinquevalent organoantimony compounds, where R=alkyl or aryl, and HL= carboxylic acid, are well-known compounds, and are obtained by the metathetical reaction from dibromo- or dichlorotrialkyl(or triaryl)antimony(V).[1,2] However, the same type compounds where the antimony bonds to the ligands through sulfur atoms are not easily synthesized. Although the organoantimony(V) compounds, such as thioglycolates,[3] monothiocarboxylates,[4] alkanethiolates,[5] and thiophenolates,[5] where the ligands bond to antimony through sulfur, have already been synthesized, their complexes of dithiocarbonate derivatives, such as dialkyldithiocarbamates, and *O*-alkyl dithiocarbonates, have not been reported yet. Meinema and Noltes[6] reported about the dialkyldithiocarbamato derivatives of the types $RSbL_2$ and R_2SbL (where R= phenyl or alkyl, and HL=dialkyldithiocarbamic acid), but they are all tervalent antimony compounds.

The authors have investigated the metathetical reaction of R_3SbBr_2 (R=methyl or phenyl) with some alkali salts of secondary amine-*N*-carbodithioic acids as well as with *O*-alkyl dithiocarbonic acids, and obtained some stable trimethylantimony(V) compounds of dithiocarbonate derivatives, although the corresponding complexes of triphenylantimony(V) could not be isolated. They are not air sensitive, and do not decompose after several weeks in a refrigerator (5 °C).

During an attempt to synthesize trialkyl(or triaryl)antimony(V) complexes of dithiocarboxy derivatives, the antimony(III) compounds of the type R_2SbL, where R=phenyl or methyl, were obtained when a little excess of the ligand was used. This fact shows that trialkyl(or triaryl)antimony(V) is readily reduced by such sulfur-containing ligands. Therefore when dibromo- or dichlorotriarylantimony(V) was treated with a large excess of dialkyldithiocarbamates, some of the aryl groups bonded to antimony were removed.

Experimental

Dibromotrimethylantimony(V) was obtained by the standard technique found in the references.[7–9] Sodium salts of piperidine- and pyrrolidine-*N*-carbodithioic acids were synthesized from each amine, carbon disulfide, and sodium hydroxide by the literature method.[10] Sodium *O*-benzyl dithiocarbonate was synthesized from benzyl alcohol, carbon disulfide, and sodium hydroxide applying the synthetic technique for other *O*-alkyl dithiocarbonates.[11,12] Potassium salts of *O*-propyl, isopropyl, and isobutyl dithiocarbonic acids were the GR of Tokyo Kasei Kogyo Co., Ltd., and other reagents were all GR of Wako Pure Chemicals Ltd. They were used without further purification.

Infrared and ^{1}H-NMR spectra were obtained using a JASCO 403G infrared spectrophotometer and a JEOL JNM-MH-100 (100 MHz) NMR spectrometer.

*Synthesis of Bis(pyrrolidine-*N*-carbodithioato)trimethylantimony(V).* To 0.96 g (3 mmol) of dibromotrimethylantimony(V) and 1.02 g (6 mmol) of soduim pyrrolidine-*N*-carbodithioate was added 20 ml of benzene–acetonitrile mixture (5/1= v/v). The mixture was stirred for about 1 h at room temperature (about 20 °C). Special air shielding was not necessary. The precipitated sodium bromide was filtered off, and the filtrate was evaporated using a water jet pump, at a temperature lower than 60 °C. After the residue thus obtained was dissolved in 7 ml of chloroform, 20 ml of petroleum ether was added, and the mixture was ice cooled. The product precipitated slowly. The yield was, on the average, 0.6 g (50%). The piperidine-*N*-carbodithioato complex was obtained by almost the same technique.

*Synthesis of Bis(*O*-benzyl dithiocarbonato)trimethylantimony(V).* To 20 ml of an isopropyl alcohol–water (1/1=v/v) mixture were added 0.96 g (3 mmol) of dibromotrimethylantimony(V) and 1.24 g (6 mmol) of sodium *O*-benzyl dithiocarbonate. The mixture was stirred for 2 h. The solvent was removed and sodium bromide was washed away with cold water. The residue was recrystallized from diethyl ether. The yield after the recrystallization was 0.9 g (58%). Other *O*-alkyl dithiocarbonates of trimethylantimony(V) were obtained by almost the same technique. However, the *O*-methyl and *O*-ethyl dithiocarbonates obtained by this process were hardly purified even by the repeated recrystallizations. As the products thus obtained decompose easily at high temperature, they must not be heated beyond 60 °C.

It should be noted that the synthetic technique used for the secondary amine-*N*-carbodithioates could not be applied for *O*-alkyl dithiocarbonates, and *vice versa*.

Results and Discussion

The elementary analyses, the calculated values from the expected chemical formulae, and melting points of these trimethylantimony(V) complexes of dithiocarbonate derivatives are shown in Table 1. All of them have the general formula $(CH_3)_3SbL_2$. These products were colorless or slightly yellow crystalline powders. All of them were soluble in organic solvents such as acetone, chloroform, and benzene, but insoluble in water.

The wave numbers of some infrared spectral bands of

TABLE 1. ANALYSES OF $(CH_3)_3SbL_2$ (%) AND THEIR MELTING POINTS

L-		C	H	N	Mp$^{a)}$(°C)
$(CH_2)_5NCS_2^-$	Calcd	36.96	6.00	5.75	
	Found	36.95	5.95	5.72	109
$(CH_2)_4NCS_2^-$	Calcd	33.99	5.49	6.10	
	Found	33.88	5.40	6.09	110
n-PrOCS$_2^-$	Calcd	30.05	5.27		
	Found	30.16	5.31		79
i-PrOCS$_2^-$	Calcd	30.05	5.27		
	Found	30.06	5.24		98
i-BuOCS$_2^-$	Calcd	33.55	5.83		
	Found	33.60	5.81		71
BzOCS$_2^-$	Calcd	42.78	4.35		
	Found	42.77	4.31		69

a) Probably decomposed at the mp or very near to it. n-Pr: $CH_3(CH_2)_2$; i-Pr: $(CH_3)_2CH$; i-Bu: $(CH_3)_2CHCH_2$; Bz: $C_6H_5CH_2$.

dithiocarboxy derivatives (organoantimony complexes and alkali salts) are shown in Table 2. In the infrared spectra of secondary amine-*N*-carbodithioates, a strong band assigned as ν(C==N) appears at about 1460 cm^{-1}, which is an intermediate wave number between 1600 cm^{-1} (for ν(C=N)) and 1100 cm^{-1} (for ν(C–N)). The wave numbers of the bands of the trimethylantimony(V) derivatives are about 20—50 cm^{-1} lower than those of the 3d transition metal dialkyldithiocarbamates,[13,14] and are almost the same as those of the alkali salts. This fact shows that the double bond character of C==N bond does not increase much when the ligand bonds to antimony.

The ν(C–N) band of both these types of compounds easily mixes with other vibrational modes. Consequently, the assignments of the bands are difficult and the opinions of many authors are controversial.[15–18] A pure ν(C=S) band should appear at about 1200 cm^{-1},[19] but, in the infrared spectra of these products, three strong bands are found in 1250—980 cm^{-1} region. The ν(C=S) bands of these complexes are easily mixed with those from other modes. The band seems to be mixed with the ν(COC) mode one in the *O*-alkyl dithiocarbonates, and with some amine ring deformational modes in the piperidine- and pyrrolidine-*N*-carbodithioates. As a result, very little information about the bond type or its strength could be obtained from the data, although the general features of these spectra clearly show that these compounds are the complexes of dithiocarbonate derivatives.

The ν(Sb–S) band is expected to appear in the 350—410 cm^{-1} region, judging from the data about trialkyl(or triaryl)antimony(V) thiocarboxylates[4] as well as about tris(alkanethiolato)antimony(III).[20] In the cases of these complexes, however, the intensity of this band is not high. The wavenumbers of the tentatively assigned peaks are about 405 cm^{-1} for secondary amine-*N*-carbodithioates and about 360 cm^{-1} for *O*-alkyl dithiocarbonates, as shown in Table 2.

A characteristic band of dibromotrimethylantimony(V) at about 867 cm^{-1}, which is assigned as the skeletal vibration $\nu(C_3Sb)$, shifts to about 850 cm^{-1} in the complexes of dithiocarbonate derivatives.

The ^{1}H-NMR spectra of trimethylantimony(V) secondary amine-*N*-carbodithioates and *O*-alkyl dithiocarbonates, as well as their alkali salts, are shown in Table 3.

The methyl proton peak of all of these complexes was a sharp singlet at room temperature, and even at −60 °C; no broadening of the peak was found during the temperature lowering. Therefore, neither the coexisting of isomers nor the existence of nonequivalent methyl groups in a organoantimony complex are probable, provided that the exchange rates of the bonding groups are low enough.

Consequently, for these complexes, the most probable structure is the penta-coordinated trigonal bipyramidal one, where three methyl groups bond from equatorial directions, and two unidentate dithiocarboxy derivative ligands from apical directions. In penta-coordinate complexes, however, Berry's pseudo-rotation may occur,[21] and in such a case the exchange of ligands in a different positions is too rapid to be distinguished by NMR, even at low temperature.[22,23] Therefore, the

TABLE 2. INFRARED SPECTRA OF $(CH_3)_3$ SbL_2 AND ALKALI SALTS OF THEIR LIGANDS (cm^{-1})

A. Secondary amine-*N*-carbodithioates.

L-		ν (C==N)	ν (C==S) and others			ν (CNC)	ν (C_3Sb)	ν (Sb–S)
$(CH_2)_5NCS_2^-$	NaL	1465	1220	1128	1002	965		
	Me_3SbL_2	1468	1223	1113	987	946	848	405
$(CH_2)_4NCS_2^-$	NaL	1455	1243	1159	992	940		
	Me_3SbL_2	1450	1243	1160	998	947	850	407

B. *O*-Alkyl dithiocarbonates.

L-		ν (C==S), ν (COC)				ν (C_3Sb)	ν (Sb–S)
n-PrOCS$_2^-$	KL	1151	1108	1058			
	Me_3SbL_2	1188	1128	1052	1036	848	365
i-PrOCS$_2^-$	KL	1180	1136	1050			
	Me_3SbL_2	1200	1139	1080—1030		846	369
i-BuOCS$_2^-$	KL	1181	1145	1105			
	Me_3SbL_2	1195	1170	1055		848	357
BzOCS$_2^-$	NaL	1227	1120	1060			
	Me_3SbL_2	1211	1158	1047		835	369

Table 3. ^{1}H-NMR of $(CH_3)_3SbL_2$ and the free ligands (alkali salts) (δ: ppm, TMS=0 or DSS=0 for $CDCl_3$ or D_2O solutions, respectively.)

L^-	ML (M=Na,K) in D_2O			$(CH_3)_3SbL_2$ in $CDCl_3$ (TMS=0)			
	L			L			CH_3
$(CH_2)_5NCS_2^-$	4.29	1.66		4.12	1.68		2.03
$(CH_2)_4NCS_2^-$	3.79	2.04		3.66	2.01		2.49
n-$PrOCS_2^-$	4.42	1.78	0.98	4.48	1.87	1.03	2.40
i-$PrOCS_2^-$	5.12	1.34		5.70		1.45	2.37
i-$BuOCS_2^-$	4.15	2.01	0.99	4.25	2.10	1.03	2.36
$BzOCS_2^-$	7.35	5.52		7.35	5.49		2.22

possibility of other penta-coordinate structures cannot be denied.

If the dithiocarboxy derivative ligands, one or both, work as the bidentates, the central antimony must be hexa- or hepta-coordinated. In such a case, the complex is expected to be rigid enough, and the exchange rate of the bonding bidentates should be low. Consequently, three methyl groups in the complex must be in unequal positions, and some splitting of the peak is expected. Some hexa-coordinated organoantimony(V) derivatives show fast pseudo-rotation even at low temperature, but even in such a case, some broadening of the peak is expected at −60 °C.[24)]

When pyrrolidine was added to a $CDCl_3$ solution of dibromotrimethylantimony(V) containing carbon disulfide, a new peak appeared at about 2.49 ppm, besides the original 2.69 ppm one, due to the formation of the pyrrolidine-*N*-carbodithioate. This peak did not disappear even when the solution was dried up and redissolved into the same solvent. On the other hand, when pyrrolidine was added to a $CDCl_3$ solution of dibromotriphenylantimony(V) containing carbon disulfide at 25 °C, one new peak at 7.30 ppm, which is likely the peak of the triphenylantimony(III) proton, appeared. When more than three times the amounts of the amine (in moles) was added to the dibromotriphenylantimony(V), the original phenyl proton peaks at 8.23 and 7.58 ppm dissapeared. This change is probably due to the reduction of organoantimony(V) to (III), owing to the instability of secondary amine-*N*-carbodithioates of triphenylantimony(V).

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