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A ^{121}Sb Mössbauer Study of Antimony Trichloride Compounds with Some Thiourea Type Ligands

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The first examples of antimony trichloride adducts with neutral ligands were reported in 1910 [1]. A number of crystal structures of adducts of this type are known [2–16] and the co-ordination geometries about antimony(III) in all of them are shown to be lone-pair distorted. The Sb sites found are of a number of types *viz.* trigonal bipyramidal with the lone-pair in the equatorial plane [2–5], ψ-octahedral, that is distorted square-pyramidal with the lone-pair in the sixth position [6–10], distorted octahedral [9–12] or complex higher co-ordinations [12]. Attempts have been made to rationalize the structures on the basis of the valence-shell electron-pair repulsion (VSEPR) model [17], but the complexity of the antimony(III) sites and the bonding involved has not been properly explained. In order to obtain further information on Sb^{III} bonding in complexes of this type we now report a study of the preparation and Sb-121 Mössbauer parameters of the following new adducts of $SbCl_3$ with thiourea type ligands, $SbCl_3$·2detu, $SbCl_3$·2diptu and $SbCl_3$·2dchtu.

The compounds were prepared by addition of the appropriate thiourea derivative (13.2 mmol) dissolved in ethanol to a solution of $SbCl_3$ (1 g, 4.4 mmol) in the same solvent. After stirring the mixtures diethyl ether was added. Yellow solids were formed with 1,3-diisopropylthiourea (diptu) and 1,3-dicyclohexylthiourea (dchtu) and a yellow oil with 1,3-diethylthiourea (detu). The yellow oil in the case of the detu adduct solidifies on standing to give a white solid. The products were purified by recrystallisation from acetone or ethanol and gave analytical data for C, H, N and Cl consistent with the formulae in Table I.

Infrared spectra (Table I) are consistent with S-coordination for detu, dchtu and diptu in the $SbCl_3$·2L compounds in that, on going from free to coordinated ligands, the ν(CN) stretching shows a positive shift, and the ν(CS) stretching a negative one on formation of an Sb–S bond. No evidence exists for the presence of free ligands in $SbCl_3$·2L compounds.

The variable temperature p.m.r. spectra of the complexes $SbCl_3$·2detu and $SbCl_3$·2diptu were obtained and the data are given in Table II. The p.m.r. spectra of the free ligand data have been interpreted by Giuliani [18] in terms of hindered rotation. Single line spectra for the CH_3, CH_2 and NH groups are found at temperatures above −60, −40 and −60 °C respectively. Below these temperatures doublet or triplet spectra are obtained because of suppression of free rotation. Giuliani explained these effects by assuming that on cooling, the isolated ligand formed hydrogen bonded dimers with a rigid configuration. The p.m.r. spectra of the complex $SbCl_3$·2detu are similar except that the coalescence temperatures are higher at about −30, −10 and −40 °C for CH_3, CH_2 and NH respectively. The higher coalescence temperatures must occur more

TABLE I. Analytical Data (Calculated Values are in Parentheses).

	M.P. (°)	Analysis (%)				$\Delta\nu$(CN) (cm^{-1})	$\Delta\nu$(CS) (cm^{-1})
		C	H	N	Cl		
$SbCl_3$·2detu	92	24.3(24.4)	4.8(4.9)	11.3(11.4)	21.6(21.6)	+44	−5
$SbCl_3$·2dchtu	110	43.1(44.0)	6.8(6.8)	7.6(7.9)	15.1(15.0)	+12	−11
$SbCl_3$·2diptu	60	31.6(30.6)	6.1(5.9)	10.4(10.2)	18.8(19.4)	+26	−5

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TABLE II. P.m.r. Data for detu, $SbCl_3\cdot 2detu$, diptu and $SbCl_3\cdot 2diptu$ δ (p.p.m. from Tetramethylsilane).

t (°)	CH_3–		–CH_2–		–NH–	
	detu	$SbCl_3\cdot 2detu$	detu	$SbCl_3\cdot 2detu$	detu	$SbCl_3\cdot 2detu$
20	1.13t	1.20t	3.49m	3.53b	6.81b	7.22b
10	1.12t	1.20t	3.49m	3.58b	6.87b	7.46b
0	1.12t	1.20t	3.49m	3.51b	6.94b	7.57b
–10	1.12t	1.20t	3.49b	3.50b 3.60b	7.00b	7.69b
–20	1.12t	1.20t	3.49b	3.37b 3.62b	7.07b	7.86b
–30	1.12t	1.19 1.27t	3.49b	3.36m 3.63m	7.15b	8.00b
–40	1.11t	1.19t 1.27t	3.23b 3.56b	3.38m 3.57m	7.22b	7.96b 8.11b
–50	1.10t	1.19t 1.26t	3.21m 3.52m	3.34m 3.60m	7.15b 7.31b 7.48b	8.02b 8.19b
–60	1.10t 1.17t	1.19t 1.27t	3.21m 3.52m	3.34m 3.62m	7.17b 7.38b 7.58b	8.10b 8.23b
–70	1.10t 1.16t	1.19t 1.26t	3.28m 3.54m	3.33m 3.62m	7.21m 7.40m 7.67m	8.17b 8.30b
–80	1.08t 1.16t	1.17t 1.24t	3.19m 3.56m	3.31m 3.61m	7.28m 7.46m 7.74m	8.21b 8.34b
	CH_3–		CH		NH	
	diptu	$SbCl_3\cdot 2diptu$	diptu	$SbCl_3\cdot 2diptu$	diptu	$SbCl_3\cdot 2diptu$
20	1.16d	1.29d	4.53m	4.31b	6.49b	7.72b
10	1.15d	1.29d	4.40m	4.10b 4.44b	6.61b	8.03b 7.62b
0	1.15d	1.29d	4.42m	4.04b 4.50b	6.64b	8.05b 7.60b
–10	1.15d	1.29d	4.44m	4.00b 4.63b	6.65b	8.06b 7.65b
–20	1.15d	1.29d	4.44b	3.99b 4.53b	6.68b	8.06b 7.73b
–30	1.15d	1.29d	4.44b	3.99b 4.53b	6.74d	8.08m 7.82m
–40	1.14d	1.29d	4.50b	3.99b 4.53b	6.80b	8.08m 7.82m
–50	1.14d	1.29d	4.53b	3.93m 4.52m	6.81b	8.02m
–60	1.12d	1.25s	4.48m	3.93b 4.50b	6.98m	8.02s
–70	–	1.25s	–	3.93m 4.50m	–	8.02s

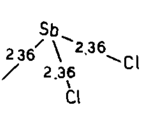
TABLE III. ^{121}Sb Mössbauer Data at 4.2 K in mm s^{-1}.

	δ^a	e^2QV_{zz}
$SbCl_3\cdot 2diptu$	–18.3(1)	–16.9(5)
$SbCl_3\cdot 2dchtu$	–17.8(1)	+9.1(5)
$SbCl_3\cdot 2detu$	–17.5(1)	+9.8(5)

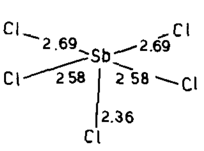
[a] Relative Ba $^{121}SnO_3$ source.

because of the presence of $SbCl_3$. This could arise for three reasons: (1) the effect of the presence of the Sb–S bond on the nature of the other bonds in the ligand (2) the possible H-bond interaction between ligand positions and the chloride atoms of the $SbCl_3$ moiety and (3) steric effects arising from the bonding requirement of the $SbCl_3\cdot 2detu$ units in the crystal lattice. Similar results have been reported for $SnCl_2\cdot 2detu$ [19]. The data for diptu are different in that the p.m.r. spectra show no evidence for the breakdown of free rotation for any of the protons studied. The spectra for the $SbCl_3\cdot 2diptu$ complex, however, do show the appearance of multiplet spectra at about 10 °C for the CH and NH protons. The appearance of doublet spectra can be interpreted in a similar fashion to those for $SbCl_3\cdot 2detu$. The data for the NH proton are of particular interest in that, after splitting, one of the types of proton bonded to N shows a shift which is almost temperature independent (typical behaviour for an intramolecular hydrogen bond), while the other proton resonance shifts downfield on cooling until the two coalesce once more.

The Mössbauer data for the thiourea adducts of $SbCl_3$ obtained by the methods previously described [20] and fitted by least-squares procedures are in Table III. Because $\Delta R/R$ for Sb-121 is negative, the chemical isomer shfts (δ) for the adducts, which have large negative values are indicative of the presence of antimony(III). The shifts are, moreover, more negative than that for $SbCl_3$ (δ = 13.7 mm s^{-1}) [21] and this is consistent with an increase in the coordination number and a decrease in the covalency of the Sb^{III} bonding on complex formation [22, 23]. Similar changes in shift to δ values of $<$15.5 mm s^{-1} on complex formation have been reported for the series of adducts $SbCl_3\cdot L$ (L = MeOH, AcOE, py, dioxane, RCONCOR, MeCN and PhCN) [24, 25] and for $SbCl_3\cdot NH_2Ph$ (δ = –16.4 mm s^{-1}) [26]. The shifts for the thiourea adducts are the most negative observed for this type of complex. This suggests that the Sb–S bonds are weaker and/or that the thiourea ligands have a greater influence on the length of the Sb–Cl bonds [22], than the other ligands that have been studied. The changes of Sb–Cl bond lengths and chemical isomer shift on complex formation can be seen by comparing the crystal structure of $SbCl_3$ [27] and $[NH_4]_2[SbCl_5]$ [7] (δ = –15.2 mm s^{-1}) [28] which contains what is effectively an $SbCl_3 \cdot 2L$ complex with L = Cl. The crystal structure of $SbCl_3$ consists of Sn in a trigonal pyramidal environment of three short Sb–Cl bonds (I) while that of $[NH_4]_2[SbCl_5]$ contains Sb in a distorted square pyramidal site(II) with one short (2.36 Å) and four longer Sb–Cl bonds (2.58–2.69 Å).



(I)



(II)

It appears to be a general feature in antimony(III) chemistry that the number of short bonds and their bond lengths, rather than the total number of bonds, largely determine the use of the Sb s-electrons and hence the chemical isomer shift [22]. Thus the three short Sb–Cl bonds in $SbCl_3$ give rise on complex formation to only one short bond (2.36 Å) in $[NH_4]_2[SbCl_5]$. For Sb^{III}–Cl systems this increase in average bond length is the main consequence of the increase in electrostatic bond character on complex formation. Assuming that the thiourea adducts have similar Sb environments to that in $[NH_4]_2[SbCl_5]$, either the Sb–S interactions must be weaker than even the longest Sb–Cl bonds and/or the shortest Sb–Cl distance in the thiourea adducts must be greater than 2.36 Å.

The thiourea adducts should show resolvable quadrupole splittings (e^2QV_{zz}) because of their low symmetry Sb environments. An excess of p-electron density in a stereochemically active lone-pair would, because of the negative value of eQ for Sb-121, give rise to a positive value for the quadrupole coupling as is found in $SbCl_3 \cdot 2dchtu$ and $SbCl_3 \cdot 2detu$. It has, however, already been pointed out [22] that the sign of the quadrupole coupling in any compound depends upon whether the p-electron density in the lone-pair is sufficiently large to dominate the electronic imbalance. In the case of $SnCl_3 \cdot 2diptu$ the direction of the principal component of the field gradient cannot, because of the negative value of e^2QV_{zz} lie in the direction of a stereochemically active lone-pair. The principal direction must instead lie in a direction that has a p-electron deficiency presumably caused by very weak interactions to the ligand.

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