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# $^{121}$Sb Mössbauer Spectra of Hexafluorocumyl Alcohol Complexes of Sb(V), and of Sb(III) with Negative Quadrupole Coupling Constants

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The antimony-121 Mössbauer spectra of antimony(V) complexes of hexafluorocumyl alcohol show that the oxygen atoms of the ligand attract 5*s* electrons of antimony atoms more than do chlorine atoms, but that the reverse is true for the $5p_z$ electrons of the antimony atoms. The antimony(III) complexes of the same ligand exhibit large negative values of $e^2qQ$, being only the second example of this negative sign.

Antimony(III) and antimony(V) complexes derived from hexafluorocumyl alcohol, $C_6H_5{\cdot}C(CF_3)_2OH$ (abbreviated as $H_2L$) have been synthesized and the crystal structures of $(Et_4N)[SbL_2]$,[1] $TolSbL_2$[2] (Tol=*p*-$CH_3{\cdot}C_6H_4$) and $SbL_2Cl$[2] have been determined. The so-called Martin ligand derived from hexafluorocumyl alcohol coordinates through O and C, thus forming a 5-membered chelate ring. In the trigonal bipyramidal (tbp) structure of $TolSbL_2$ and $SbL_2Cl$, the electronegative oxygen atoms occupy the apical positions and the electropositive aromatic carbon atoms equatorial positions. The stabilization of the tbp structure around the main-group elements such as Si, P, S, Sn, Sb, Te, I and Bi in the hexafluorocumyl alcohol complexes is attributed to the enhanced electronegativity of the oxygen atom by the electron-attracting $CF_3$ groups and the chelating effect.

Antimony-121 Mössbauer spectroscopy is a useful technique for elucidating the structure and bonding of the antimony compounds. To determine the extent of the electron-withdrawing power of the oxygen atom of the Martin ligand compared to the halogen atoms, we undertook a Mössbauer spectroscopic study of a series of antimony(V) hexafluorocumyl alcohol complexes in which the set of apical atoms are varied ($Tol_2SbLX$: O-F, O-Cl, O-Br, O-I and $TolSbL_2$: O-O) and also a similar study of two antimony(III) hexafluorocumyl alcohol complexes.

$Tol_2SbLX$ (X=F, Cl, Br, I),[3] $TolSbL_2$, TolSbL,[3] and $(Et_4N)[SbL_2]$ were prepared by methods described in the literature or analogous methods. Antimony-121 Mössbauer spectra were obtained by an Austin Science S-600 Mössbauer spectrometer using a $Ca^{121m}SnO_3$ source (16 MBq) and a pure germanium detector. Both the source and the samples containing 15 mgSb cm$^{-2}$ were kept at 20 K in a cryostat incorporating a closed-cycle

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Table 1. $^{121}$Sb Mössbauer parameters at 20 K

| Compound | $\delta$[a)] / mm s$^{-1}$ | $e^2qQ$ / mm s$^{-1}$ | $\eta$ | $\Gamma$ / mm s$^{-1}$ |
|---|---|---|---|---|
| $TolSbL_2$ | 4.16 | -18.3 | 0.15 | 2.50 |
| $Tol_2SbLF$ | 4.26 | -20.2 | 0.05 | 2.45 |
| $Tol_2SbLCl$ | 3.59 | -19.2 | 0.23 | 2.94 |
| $Tol_2SbLBr$ | 3.36 | -18.4 | 0.08 | 2.45 |
| $Tol_2SbLI$ | 3.32 | -16.6 | 0.31 | 2.73 |
| TolSbL | -2.24 | -27.6 | 0.79 | 2.48 |
| $(Et_4N)[SbL_2]$ | -1.37 | -24.9 | 0.84 | 2.52 |
| $Ph_3Sb$ | -0.81 | 16.7 | 0.0 | 2.83 |

a) relative to InSb at 20 K.

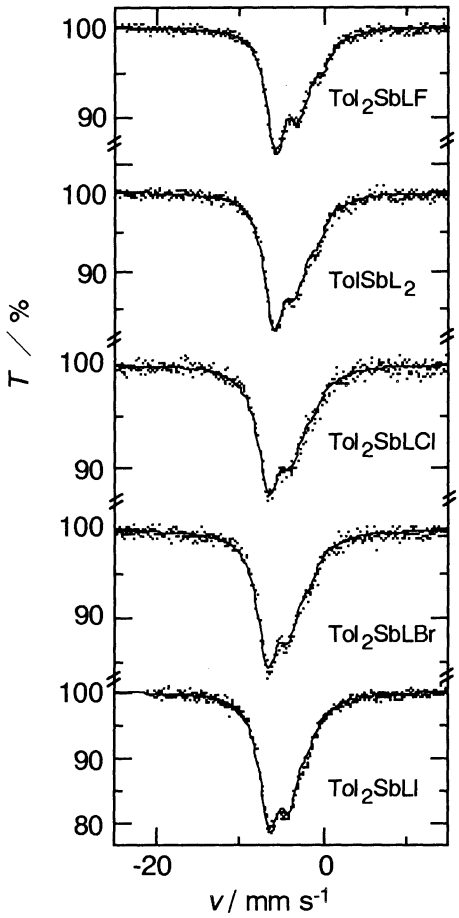



Fig. 1. Mössbauer spectra at 20 K for antimony(V) complexes, $Tol_2SbLX$ and $TolSbL_2$.

refrigerator.[4] The spectra were computer-fitted to a twelve-line quadrupole-split pattern using a transmission integral method.[5] The results are shown in Fig. 1, Fig. 2, and Table 1. The isomer shifts in Table 1 are given relative to InSb at 20 K.

From the top to the bottom in Fig. 1, the isomer shift ($\delta$) decreases, which corresponds to the increase in the *s* electron density at the antimony nucleus. The $\delta$ values listed in Table 1 decrease monotonically as the halogen changes from F to I, the order coinciding with that in the electronegativity. The asymmetric shape of the absorption peaks in Fig. 1 clearly shows that the sign of the quadrupole coupling constant ($e^2qQ$) is negative, which means that 5*p* electron density is greater in the *xy* (equatorial) plane than in the *z* direction corresponding to the apical bonds in the tbp molecule.

Fig. 3 shows the plots of $\delta$ and $e^2qQ$ observed for the complexes having one common oxygen atom at the apical position against the Pauling's electronegativity[6] of the another apical atom. As the electronegativity of the apical atom increases, the $\delta$ value increases, showing the corresponding decrease in the *s* electron density at the antimony nucleus. This implies the withdrawal of *s* electrons from Sb along the apical bonds. Likewise the value of $|e^2qQ|$ increases as the electronegativity of the halogen atoms increases, suggesting that the electrons in the $5p_z$ orbital of Sb are withdrawn toward the halogen atom along the apical Sb-X bond.

It is surprising that the $|e^2qQ|$ value of $TolSbL_2$ with two apical O atoms is lower than that for $Tol_2SbLCl$ with O and Cl atoms in apical position. The oxygen atom seems not to withdraw so much 5*p* electron density from antimony as expected from its large electronegativity. So we can say that the apical atoms's withdrawing power of $5p_z$ electrons from the antimony atoms along the apical direction decreases in the order, F>Cl>Br>O>I, while the withdrawing power for the 5*s* electrons decreases in the order, F>O>Cl>Br>I. The negative sign of

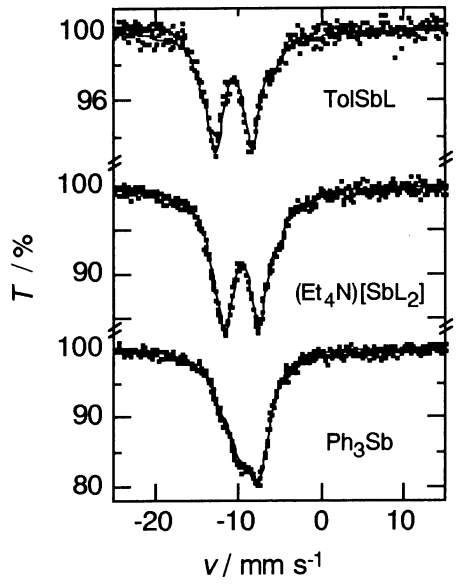



Fig. 2. Mössbauer spectra of Antimony(III) complexes at 20 K.

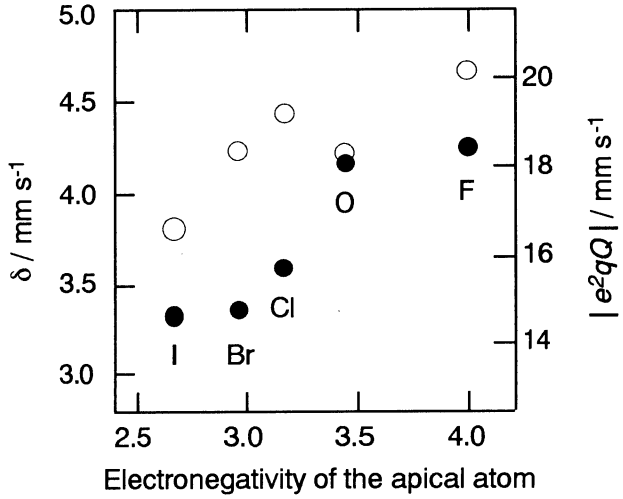



Fig. 3. Plots of isomer shift (●) and quadrupole coupling constant (○) against electronegativity of the apical atom for $TolSbL_2$ and $Tol_2SbLX$(X=F, Cl, Br, I).

the $e^2qQ$ can readily be explained since electronegative apical atoms preferentially attract $5p_z$ electrons of antimony, thereby enhancing the relative $5p$ electron population of antimony in the $xy$ plane.

$^{127}$I Mössbauer spectra at 20 K of $Tol_2SbLI$ gave the $\delta$=-0.16 mm s$^{-1}$ (relative to KI at 20 K), and $e^2qQ$=-21.2 mm s$^{-1}$, suggesting that the iodine electron configuration is $5s^{1.98}\ 5p_x^{2.00}\ 5p_y^{2.00}\ 5p_z^{1.56}$ and the charge on iodine atom -0.54 $e$.[7] This shows that an apical Sb-I bond is mainly composed of Sb($5s$)- I($5p_z$) and Sb($5p_z$)- I($5p_z$).

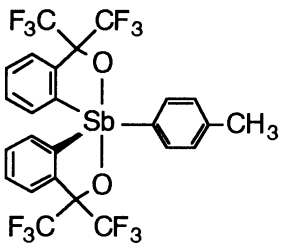
In summary, in the solid Sb(V) complexes of hexafluorocumyl alcohol the oxygen coordinating atom attracts 5s electrons of antimony as expected from its electronegativity, but withdraws less $5p$ electrons of antimony than expected from its electronegativity.

The spectrum of triphenylantimony(III), $Ph_3Sb$ in Fig. 2 shows steep descent on the less negative velocity side and gradual ascent on the more negative velocity side, which is typical for the antimony(III) with positive $e^2qQ$. In contrast, the two hexafluorocumyl alcohol complexes give well resolved spectra whose computer curve fitting gave large negative values of $e^2qQ$ and large values of the asymmetry parameter, $\eta$ as seen in Table 1.

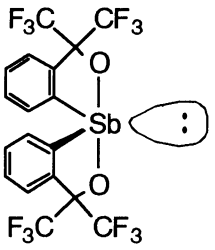
The negative $\delta$ shows that the oxidation number of antimony in each compound is +3. In antimony(III) compounds, the sign of $e^2qQ$ is normally positive since the direction of the $z$ axis of the electric field gradient (EFG) at the antimony nucleus coincides with that of the lone pair having a $p$-orbital character.[8] The negative sign of $e^2qQ$ observed for TolSbL is the second observation among the many Sb(III) compounds studied so far. The first one was done for dimethylchloroantimony(III), $(CH_3)_2SbCl$ ($\delta$=-2.5 mm s$^{-1}$, $e^2qQ$=-31.7 mm s$^{-1}$, $\eta$=0.77).[9] A common structural feature for the two compounds is that the antimony(III) atoms are surrounded trigonalpyramidaly by two electron-donating atoms and one electron-withdrawing atom. If we include the non-bonding electrons, then both compounds have pseudo-tetrahedral coordination.

A rare negative $e^2qQ$ was found also in $(Et_4N)[SbL_2]$ whose structure is pseudo-trigonal bipyramidal

including the lone pair of electrons. It is clear that the 5*p* electron density is rich in the equatorial plane (*xy* plane) due to the lone pair and the electrons from the phenyl group, thus implying that the *z* axis of the EFG is along the apical direction. It is reasonable to have the same negative sign of $e^2qQ$ for $(Et_4N)[SbL_2]$ and $TolSbL_2$ which has a tolyl group on the equatorial position instead of the lone pair. The more negative δ and $e^2qQ$ values of $[SbL_2]^-$ when compared to the values for $[TolSbL_2]$ clearly show that the lone pair of electrons in $[Sb(III)L_2]^-$ make the Sb atom larger in 5*s* electron density as well as 5*p* electron density in the *xy* plane than the Sb-C(Tol) bonding electrons do in $[TolSb(V)L_2]$.




[TolSbL2]




$[SbL_2]^-$

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