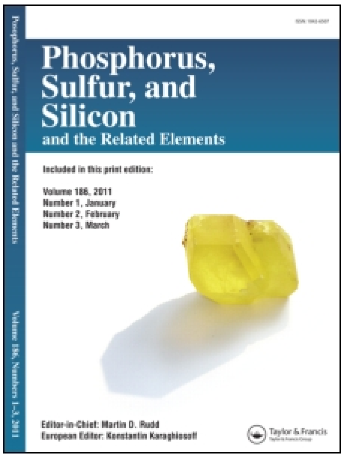

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COMMUNICATION. OBSERVATIONS ON THE 121-Sb MÖSSBAUER PARAMETERS OF ANTIMONY (III) COMPOUNDS FEATURING A PYRAMIDAL SbS_3 SKELETAL UNIT

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Communication

OBSERVATIONS ON THE 121-Sb MÖSSBAUER PARAMETERS OF ANTIMONY (III) COMPOUNDS FEATURING A PYRAMIDAL SbS_3 SKELETAL UNIT

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A linear correlation between the chemical isomer shift and the quadrupole coupling constant for a number of antimony tris-thiolates has been evidenced. This behaviour can be rationalized on considering a modulation of the s/p character of the lone pair of electrons from the influence of secondary bonds.

Key words: Structure; secondary bonds; lone pair.

Bond lengths which are well within the sum of the appropriate van der Waals radii but longer than those representative of normal single bonds are frequently encountered in antimony(III) compounds. Often the occurrence of these (secondary) bonds can be unambiguously assessed only through the x-ray structure determination of a given compound and structural data are often needed in order to interpret the results from other spectroscopic techniques. This appears to be the case of antimony tris-derivatives with potentially bidentate monoanionic ligands having SX (X = S, O, N) donor atoms whose structure is normally based on a pyramidal SbS_3 primary unit while the X donor atoms provide a variable network of secondary bonding interactions. Examining the available 121-Sb Mössbauer spectroscopic results, both from literature sources[1–3] as well as from our own measurements, we have noticed that a number of tris-thio-derivatives of the type above are showing a correlation between the chemical isomer shift (IS) and the quadrupole coupling constant (eQV_{zz}) which can be extended to simple tris-thiolates, $Sb(SR)_3$, and to a compound of different chemical nature such as SbSI. Data are collected in Table I and Figure 1 shows the concomitant variation of both parameters, the spanned ranges being indicative of substantial electronic changes in the antimony valence shell.

The interpretation of the relationship, which is linear to a good approximation ($r = 0.98$), simply considers here that both IS and eQV_{zz} are mainly governed by

TABLE I

121-Sb Mössbauer parameters

Compound	IS[a] mm/s	eQV_{zz} mm/s	Reference
1 SbSI	− 15.4 ± 0.01	6.9 ± 0.1	[1]
2 $Sb(S_2CNEt_2)_3$	− 15.3 ± 0.1	7.8 ± 1	[2]
3 $Sb(SOCCH_3)_3$	− 14.8 ± 0.2	8.9 ± 0.5	this work
4 $Sb(SC_6H_4NH_2)_3$	− 14.3 ± 0.2	10.0 ± 0.5	this work
5 $Sb(SC_3H_6O_2N)_3$[b]	− 14.2 ± 0.2	10.3 ± 0.5	this work
6 $Sb(SC_6H_4Br—p)_3$	− 12.8 ± 0.1	13.4 ± 0.2	[3]
7 $Sb(SC_6H_4R—p)_3$[c]	− 12.3 ± 0.1	13.7 ± 0.2	[3]

[a] Isomer shift relative to Ca $^{119m}SnO_3$.
[b] $\eta = 0.37$.
[c] Average values for R = Me, Bu.

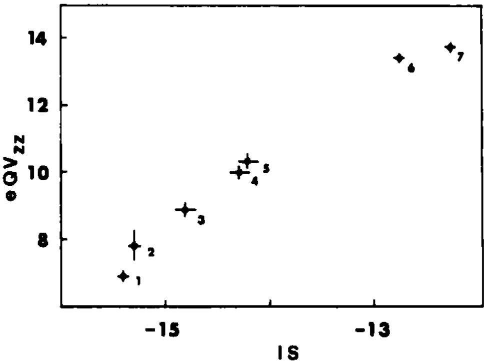

FIGURE 1 121-Sb eQV_{zz} versus IS values for compounds in the table.

the s/p character of the lone pair of electrons (E) which, in turn, is modulated by the secondary bonding network.

For all complexes the sign of eQV_{zz} is positive (V_{zz} is thus negative) indicating an imbalance in the antimony 5p orbital occupation with an excess of *p* electron density in the direction of the electric field gradient (e.f.g.) principal axis. The largest eQV_{zz} values are encountered with compounds of the type **6** and **7** in which the nature of groups bonded to antimony induce to assume the lacking of secondary bonding interactions. The coordination about antimony in these compounds can be expected to feature an idealized C_{3v} SbS_3E unit with SSbS angles close to 90°. Such disposition of the SbS bonds is expected to provide a small contribution to e.f.g. so that the measured V_{zz} value is probably reflecting the contribution of E alone.

The x-ray structures for diethyldithiocarbamate **2** and monothioacetate **3**,[4,5] besides showing a distorted pyramidal SbS_3 "primary" skeleton, having mean SSbS angles approaching 90°, give also evidence of a "secondary" bonding network which is provided by the anisobidentate chelation from the ligand together with even weaker Sb..X intermolecular contacts. The reduced eQV_{zz} value for these compounds could be rationalized in terms of point charge model arguments by considering that, due to the small ligand bite angle, the SbX bonds are mainly insisting on the xy plane thus providing subtractive terms to V_{zz} while the dominant contribution to this latter is still expected to derive from E. However, the sensible increase in the s-density at Sb denounced by the smaller IS value is not explained by a mechanism which sees simply the electron donation from secondary donors in the antimony p-orbitals but suggests that Sb(III) non-bonding electrons have also gained in s-character at expences, conceivably, of SbS primary bonds.

The lowest IS and eQV_{zz} values considered here are those recently reported for SbSI **1**. An SbS_3 primary coordination can be recognized in the structure of this compound which, being polymeric in nature, actually presents two bridging sulfurs and a shorter third SbS bond. A stereoactive E would be more likely located opposite to this shortest bond; however, there are four iodine atoms which complete the Sb coordination sphere (all at distances larger than the sum of the ionic radii) conceivably reducing the stereoactivity of E enhancing its s-character.

Although available structural data are too limited in order to assess a clear relationship between an "efficiency" of the secondary bonding network and spectroscopic parameters, a structural detail such as the decrease of the mean SbS bond distance on going from **1** to **3** (261, 250 and 247 pm, respectively) gives some support to the view that E is becoming more stereoactive in the same order.

The location in the mean section of the plot of compounds **4** and **5** is here interpreted as indicating that antimony is experiencing an intermediate situation in which secondary bonding interactions can still be present, although considerably weakened. The 2-mercaptoaniline ligand in **4**, and cysteine in **5**, both bear appropriate additional N and/or O donor centers whose coordination has been excluded on the basis of infrared results.[6,7] However, these groups are presumably in the proximity (below Van der Waals distances) of the antimony atom rendering its environment, i.e., the environment of E, different from the "empty space" expected in the case of compounds of the type **6** and **7**.

EXPERIMENTAL

Samples of antimony(III) tris-thioacetate, tris-2-mercaptoaniline and tris-cysteinate, were prepared according to published procedures[4,6,7] and their identity checked through elemental analysis and infrared spectra.

The ^{121}Sb Mössbauer spectra of **3–5** were measured with both source (Ca $^{121m}SnO_3$, nominally 0.5 mCi) and absorber at liquid nitrogen temperature. Each absorber, containing 8–10 mg Sb per cm^{2}, was prepared by mixing the appropriate amount of ground compound with silicon grease and hold between aluminum foils. Data acquisition, calibration and fitting procedures were as elsewhere reported.[8]

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