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Preliminary communication

ANTIMONY-121 MÖSSBAUER SPECTRA OF SOME TRIPHENYLANTIMONATE(V) SCHIFF BASE COMPLEXES

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Summary

The ^{121}Sb Mössbauer spectra at 9 and 78 K of R_3Sb-Schiff base complexes which do not have trigonal bipyramidal structures are discussed, and a *mer*-octahedral structure is proposed.

Mössbauer measurements utilizing the 37-keV transition in ^{121}Sb have been reported for several organoantimony compounds of the types R_4SbX and R_3SbX_2 (X = various electronegative groups) [1 5], which have trigonal bipyramidal (TBP) structures with X occupying one or both apical positions. Such data are also available for some neutral [6] and cationic [7] derivatives containing Fe- Sb σ-bonds and in which the antimony atom is in a distorted tetrahedral environment. Very recently, Mössbauer data for a number of octahedral $RSbX_5$ and R_2SbX_4 complexes have been published [8], and we have verified [9] the expected $-1/2$ quadrupole coupling constant ratio in the respectively *cis*- and *trans*-octahedral complexes Ph_2SbCl_2(oxin) and Ph_2SbCl_2(acac) (oxin = 8-hydroxyquinolinate, acac = acetylacetonate). We present here ^{121}Sb Mössbauer data obtained in a preliminary study of complexes of the types R_3SbX(oxin) and R_3SbL (L = anion of a potentially terdentate Schiff base). These are the first Mössbauer data to be reported for triorganoantimony(V) derivatives which do not possess the usual TBP configuration with three equatorial Sb—C bonds (*eq*-TBP).

Ph_3SbCl(oxin), Ph_3Sb(Sab) and Ph_3Sb(MeSab) (H_2Sab = Ia, H_2MeSab = Ib) were prepared by treatment of Ph_3SbCl_2 with the sodium salt of the appropriate ligand as described previously [10, 11]. All three yellow complexes gave correct elemental analyses; melting points and IR spectra were in agreement with literature data [10, 11]. Mössbauer spectra were recorded with thin (8—10 mg Sb/cm^2) carefully ground absorbers maintained at ~9 K, and the 1 mCi $Ba^{121m}SnO_3$ source at ~78 K. The spectra were fitted by a programme described elsewhere [4, 7].

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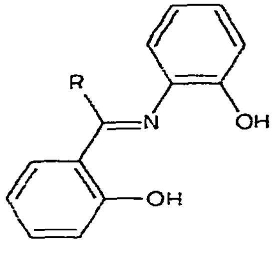

(Ia : R = H (H_2Sab); Ib : R = Me(H_2MeSab))

(I)

The three complexes gave very similar Mössbauer spectra, with quadrupole coupling constants e^2qQ in the range −16 to −18 mm/s, and in every case the asymmetry parameter η of the electric field gradient (EFG) was close to unity (Table 1, Fig. 1). These data clearly establish that the structure(s) adopted here is not the *eq*-TBP one normally found [1—5] for triorganoantimony complexes, since in this case η would not differ sensibly from zero [4, 5]. They also rule out a *fac*-octahedral structure, which would show little or no quadrupole interaction [12].

TABLE 1

^{121}Sb MÖSSBAUER PARAMETERS[a]

Compound[b]	δ (ppm)[c]	e^2qQ (mm/s)[d,f]	Γ (mm/s)[e]	η
Ph_3SbCl(oxin)	−4.58±0.05	−17.8±0.6	2.82±0.06	0.83±0.05
Ph_3Sb(Sab)	−3.82±0.05	−18.0±0.5	2.84±0.08	0.83±0.08
Ph_3Sb(MeSab)	−3.71±0.05	−16.7±0.4	2.86±0.08	0.93±0.07

[a] Data recorded with source ~78 K and absorbers at ~9 K. [b] See text for ligand abbreviations. [c] Isomer shift relative to $Ba^{121m}SnO_3$. [d] Values of $|e^2qQ|$ in mm/s calculated for various structures from the additive EFG model are: *mer*-octahedral, 19.3; *mer*-TBP, 16.3; *cis*-TBP, 11.5; these values should be accurate to ± 3 mm/s [13]. [e] Full line width at half maximum. [f] $Q_e/Q_g = 1.34$; $Q_g = -0.28 \times 10^{-28}$ m^2.

There are three other possible structures for these complexes: If the Schiff bases I are terdentate and oxine bidentate, *mer*-octahedral structures will be obtained, whereas if these ligands are bi- and monodentate, respectively, either a *cis*- or *mer*-TBP structure will be found. We can use the additive EFG model [4, 13] and partial quadrupole splitting parameters for five- and six-coordinate [13—15] antimony(V) to predict $|e^2qQ|$ values for these three structures. (Signs of e^2qQ from additive model treatments are not always reliable when η is large [13]). The predicted values are given in Table 1.

At any realistic tolerance limit [13] these calculations preclude a *cis*-TBP structure. However, the Mössbauer data are compatible with either of the other alternatives, and do not appear capable of distinguishing convincingly between them. Although the phenyl groups definitely appear to adopt a meridional configuration, the precise structural type obviously depends on whether the bases exercise their coordinating capacity fully or partially.

The ability of Ia to function as a terdentate ligand has been established by ^{119}Sn Mössbauer [12, 16] and X-ray crystallographic [17] studies of Ph_3Sn(HSab) and Me_2Sn(Sab); moreover, Me_3Sb(Sab) has been shown [11] to have a *mer*-

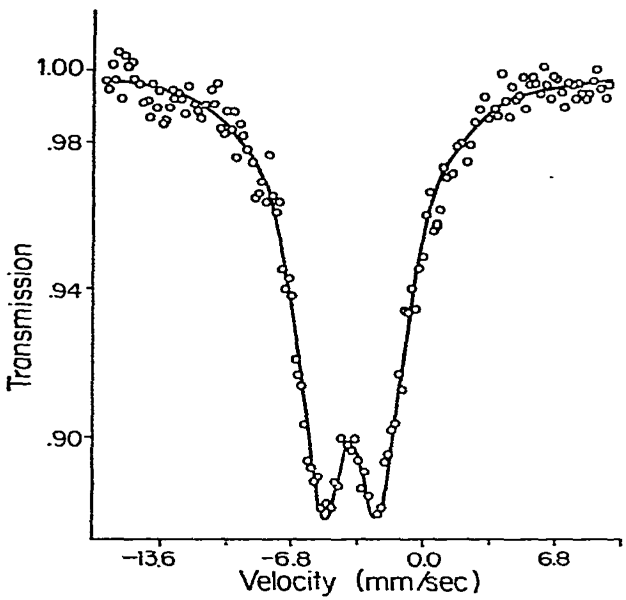

Fig. 1. ^{121}Sb Mössbauer spectrum of $Ph_3Sb(MeSab)$ at 9 K.

octahedral structure with the ligand terdentate and quasi-planar. In the IR spectrum of solid $Ph_3Sb(Sab)$ a very strong band attributable to $\nu(C{=}N)$ is found at 1610 cm^{-1}, compared to 1630 cm^{-1} in the free ligand [11]. This shift of $\nu(C{=}N)$ to lower energy in metal complexes of Sab^{2-} has been interpreted [11, 18] in terms of M—N coordination, with the ligand terdentate. Moreover, the UV spectrum of $Ph_3Sb(Sab)$ is entirely similar to that of $Me_3Sb(Sab)$ [11], in which the ligand is known to be terdentate. Such indirect evidence favours a *mer*-octahedral structure for $Ph_3Sb(Sab)$, and presumably $Ph_3Sb(MeSab)$.

This same structural type is almost certainly adopted by $Ph_3SbCl(oxin)$ in the solid state*. If oxine were monodentate rather than chelating, the ligand arrangement would be expected to follow Bent's rule [19] with the more electronegative ligands at the apical positions of a trigonal bipyramid. Such an *eq*-TBP structure is ruled out by the Mössbauer data (vide supra), and a *mer*-octahedral structure with a chelating oxine group is indicated.

Further work on other triorganoantimony compounds which are likely to be hexacoordinate is in progress.

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*Solution UV spectra of this complex suggest the oxine ligand is chelating in benzine but monodentate in ethanol and chloroform [10].

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