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Mössbauer Studies on Tin(IV) and Organotin(IV) Diacetylbis(Benzoylhydrazone) Complexes

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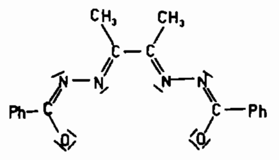
The Mössbauer parameters of Ph_2SnDB, $PhClSnDB$ and $Sn(DB)_2$ were determined, where DB^{2-} is the dianion of the multidentate ligand diacetylbis(benzoylhydrazone). According also to data treatment with the point charge model formalism, the configurations of Ph_2Sn^{IV} and $PhSn^{IV}$ derivatives appear to be essentially octahedral, with linear CSnC and CSnCl skeletons. As to $Sn(DB)_2$, it appears that the electrical charge density at the Sn^{IV} nucleus has a cubic symmetry, which is consistent with both tetrahedral and octahedral configurations around Sn^{IV}.

Introduction

It is well known that the Schiff base diacetylbis(benzoylhydrazone), in its dianion form I (= DB^{2-}), acts



I

as a multidentate base towards metals ions.[1–6] Several novel complexes of DB^{2-} with lead and tin metal and organometal cations were recently prepared, and hypotheses were advanced on their configurations.[7,8] This paper reports a subsequent Mössbauer study on $Sn(DB)_2$, Ph_2SnDB and PhClSnDB, which was devoted to gain a definite knowledge of the nature of these compounds in the solid state.

Experimental

The ligand H_2DB and its complexes $Sn(DB)_2$, PhClSnDB and Ph_2SnDB were obtained as reported previously.[7,8] The Mössbauer spectra were determined on samples held at liquid N_2 temperature in a AERE (Harwell) criyostat with a $Ba^{119}SnO_3$ source (NEN), at constant acceleration (triangular waveform), using the Elscint–Laben spectrometer described earlier.[9] Velocity calibration was effected by means of 99.9% iron foil spectra obtained with a ^{57}Co source (NEN). The zero point of the Doppler velocity scale was determined with respect to room temperature $BaSnO_3$–$BaSnO_3$ absorption spectra. The obtained data were reduced by a computer fitting program based on Lorentzian curves.[9] The Mössbauer parameters are reported in Table I; typical spectra are shown in Fig. 1 (a, b).

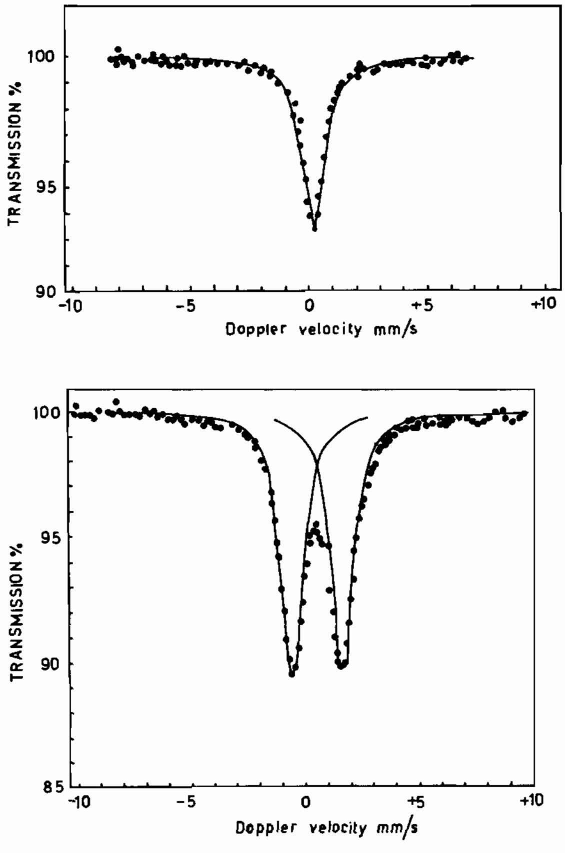


Figure 1. Mössbauer spectra of $Sn(DB)_2$ (a) and PhClSnDB (b). Solid lines are computed Lorentzians.

TABLE I. Mössbauer Parameters (mm s^{-1}), and Point-Charge Calculations.

Compound	δ^a	ΔE^b	$\Gamma^{+\,c}$	$\Gamma^{-\,c}$	([L]–[Cl])^e	$\Delta E_{calcd.}{}^h$
Ph_2SnDB	1.17	3.40	0.95	1.05	+0.10	
PhClSnDB	0.56	2.12	1.20	1.20	−0.05^f	+1.50^f
					−0.19^g	+1.80^g
$Sn(DB)_2$	0.19	0	1.00^d			

[a] Isomer shift wich respect to R.T. $BaSnO_3$ spectra. [b] Experimental values of quadrupole splitting. [c] Full width at half height of the resonant peaks; the positive and negative subscripts refer to the doublet components at greater and lesser velocity than the spectrum centroid, respectively. [d] Γ_{av} of the single peak. [e] Calculated partial quadrupole splittings due to ligand atoms, see text. [f] From Eq. (2), *trans*-PhCl. [g] From Eq. (3), *cis*-PhCl. [h] Using ([L]–[Cl]) = +0.10 mm s^{-1}.

Discussion

The observed increase of the isomer shift, δ^{10} (Table I), from $Sn(DB)_2$ to PhClSnDB and Ph_2SnDB reflects the increases in the s electron densities at the tin nucleus due to the occurrence of one and two C–Sn bonds respectively, in the organotin derivatives. The δ value of $Sn(DB)_2$ correlates well to those of complexes where tin(IV) is tetrahedrally coordinated by oxygen atoms (δ = 0.20–0.40 mm s^{-1})[11] while δ of PhClSnDB lies within the range typical of RSn^{IV} bound to O,N donor atoms.[12–15] As to Ph_2SnDB, its δ value is a bit too low than expected for a regular *trans*-R_2 octahedral structure,[11] which implies a distorted configuration for this complex.

The compound $Sn(DB)_2$ shows a single line spectrum (Fig. 1a) where Γ is sufficiently narrow (Table I) to exclude the occurrence of an unsplit doublet, which is consistent with a cubic charge symmetry around the Sn^{IV} nucleus.[10,11] This could be originated by the tetrahedral structure previously advanced, where the ligand would act as bidentate,[7,8] as well as by an octahedral configuration with tridentate DB^{2-}. It is interesting to point out that $Sn(DB)_2$ does not show any room temperature effect, which would exclude the occurrence of polymerization in the solid state[16] and supports molecular structures of the type discussed above.

The quadrupole splitting, ΔE^{10}, of Ph_2SnDB suggests a *trans*-R_2 octahedral configuration,[11] perhaps distorted, where DB^{2-} would behave as a tetradentate "planar" ligand.[7,8] The absence of room temperature effect[16] for Ph_2SnDB and PhClSnDB rules out polymeric structures also for these compounds. The ΔE's of RSn^{IV} derivatives are theoretically almost independent from coordination number and structure (see point-charge model equations of ΔE for 4,5 and 6 coordinated RSn^{IV} [17]) so that no unequivocal structural informations would be obtained in these cases from experimental ΔE values.[18] On the other hand, by taking into account the greater Lewis acidity of RSn^{IV} with respect to R_2Sn^{IV}, it is very reasonable to assume that DB^{2-} in PhClSnDB acts as tetradentate, analogously to the findings concerning Ph_2SnDB. An octahedral type structure could be then advanced also for PhClSnDB, where the PhSnCl moiety would in principle assume a linear (*trans*-PhCl) or bent (*cis*-PhCl) configuration. In order to possibly solve this uncertainty, and check the hypotheses above, point-charge model calculations[11,17,19] of ΔE were carried out on Ph_2SnDB and PhClSnDB, supposed to be regular octahedral species. The respective point-charge Eqns. are as follows[11,17,19] ([L] = [DB]/4):

Ph_2SnDB, *trans*-Ph_2:

$$\Delta E = 4([R]-[Cl]) - 4([L]-[Cl]) \quad (1)$$

PhClSnDB, *trans*-PhCl:

$$\Delta E = 2([R]-[Cl]) - 4([L]-[Cl]) \quad (2)$$

PhClSnDB, *cis*-PhCl:

$$\Delta E = 2\{([R]-[Cl])^2 + ([L]-[Cl])^2 - ([R]-[Cl])([L]-[Cl])\}^{1/2} \quad (3)$$

where the terms ([R]–[Cl]) are partial quadrupole splittings,[19] p.q.s.; taking ([R]–[Cl]) = +0.95 mm s^{-1},[19] and the principal (z) axis of the electric field gradient tensor[20] coincident with C–Sn–C and Sn–C bond directions in Ph_2SnDB and PhClSnDB respectively (which implies that ΔE is positive for all configurations here studied[11,19]), the p.q.s. ([L]–[Cl]) of Table I were calculated from experimental ΔE's and Eqns. (1)–(3). It appears from Table I that ([L]–[Cl]) of PhClSnDB, *trans*-PhCl, is reasonably consistent with the corresponding p.q.s. from Ph_2SnDB, while that from *cis*-PhCl is out the accepted range;[19] the latter configuration would be then ruled out.

In this context it must be taken into account that opposite conclusions would be extracted by ΔE's calculated by Eqns. (2) and (3), using ([L]–[Cl]) = + 0.10 mm s^{-1} (Table I). This inconsistency is clearly originated by the high positive value of ([L]–[Cl]), due to the rather low experimental ΔE of the estimator Ph_2SnDB on the hypothesis of a *trans*-Ph_2 octahedral structure.[11,19] The latter circumstance is indicative of distortion from the idealized configuration to which refers Eq. (1), so that Ph_2SnDB cannot be taken as the sole estimator of ([L]–[Cl]), and the only way to obtain structural answers by the point-charge model formalism is to compare p.q.s. values computed for various compounds in different configurations.

Acknowledgements

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