General comments on presentation:

Cover: include a space between: Department" and "of":
This is a printing mistake. However, inside page of the thesis is correct.

The titles of Chapters 3 – 5 have a spelling error; see also pp ii-iii:
Corrected as suggested.

The alignment of the text on p. 101 is awry. "et. al." must be presented in the correct form, i.e., "et al."
Corrected as suggested.

"cf" must be presented in the correct form, i.e., "cf."
Corrected as suggested.

The crystallographic study shows... {p. 5}:
Corrected as suggested.

"report is" should be "report is of" {p. 11}:
Corrected as suggested.

"solid state" should be "solid-state" {p. 11} and elsewhere in the thesis: Corrected as suggested (p. 11, 46, 90, 125, 151).
"...of a few triorganotin(IV)" on p. 12 – triorganotin(IV) what? :
Corrected as suggested.
"the activity" should be "their activity" {p. 14}:
Not found in p. 14, but found in p. 13 and corrected.

"specific comments" should be "specific comment" {41}:
Corrected as suggested.
"in situ" should be "in situ":
not changed since both the conventions are used.
Specific comments/queries:

CHAPTER 2

T 2.2: Why are Rint, R(F) and wR(F2) given to four decimal places for L3? Three for the residual electron density is also incorrect. See also Table 3.7; here, 2theta values need to be given to one decimal place. See also T 5.2 {p. 131}:

Errors were corrected for L3 for Rint, R(F), wR(F2) and also for the residual electron density and, now recorded to three decimal places {p. 27}. 2 theta values given in Table 3.7 / 5.2 are as per chemistry journal specifications and hence not changed.

p. 29: The carboxylate acid molecule [sic.] can not be a zwitterion – be more precise and in naming the compound as this is ambiguous – specify the compound as L3 and then discuss the zwitterionic nature of the N/OH group.

The carboxylic acid molecule i.e. L2HH’ is zwitterion as evident from the electron density peak associated with the expected phenolic H atom and was found to be closer to the imine N-atom. The reviewer has mistaken L2HH’ with L1HH’ (see p.29).

p. 32: “Two dimensional network” is an incorrect description – a network is 3D – 2D layer or 2D array is correct.

Two dimensional network and 2D array reflect the same presentation and any of the presentations can be used and, hence not changed.

p. 33: there is no four-fold axis in the monoclinic unit cell

Query cited is not found in the text.

p. 38: the treatment of the H atoms in the refinements as given is inconsistent with the data listed in Table 2.4 to 2.6 that shows that some H atoms had been refined.

H-atoms were placed in the positions indicated by a difference electron density map and their positions were allowed to refine together with individual isotropic displacement parameters and hence the data is consistent with the data listed in Tables 2.4 to 2.6. Reviewer over looked to see the experimental details.
CHAPTER 3

How can the geometric parameters for 1 be equivalent to those of 4 if they are different structures? {p. 57} A reference to the source of the van der Waals radii should be given {p. 57}

The complexes 1 and 4 are tributyltin(IV) compounds of the same series where the ligands are different. This is reflected in the crystallographic parameters (refer to Table 3.7), for example, In compound 1, the crystal system is triclinic and the space group is $P\overline{1}$ while in compound 4, the crystal system is monoclinic and the space group is $P2_1/n$, and all other unit cell parameters are also different, as expected. However, the geometric parameters are of the order of same magnitude except for some which are clearly discussed in the text (see p.63). A reference to the source of van der Waals radii is excluded as this is very common and hence the reference is excluded.

Why is the inclusion of NMR and Mössbauer data “convenience of discussion”? {p 64}

The compound Ph$_3$SnL$_1$H.OH$_2$ was reported earlier by our group (T.S. Basu Baul, S.M. Pyke, K.K. Sarma, E.R.T.Tiekink, Main Gr. Met. Chem., 19 (1996) 807, this reference is also cited in this chapter i.e. ref. No. 33). The previous paper reports only $^1$H & $^{13}$C and X-ray structure of the complex. This compound was used as one of the starting materials for obtaining other derivatives, e.g. complexes 2-5. Since all the triphenyltin complexes (2-5) of present investigation were investigated by $^{119}$Sn NMR, ESI-MS and Mossbauer spectroscopy and hence the starting triphenyltin compound i.e. Ph$_3$SnL$_1$H.OH$_2$ (1) was also investigated by the $^{119}$Sn NMR, ESI-MS and Mossbauer spectroscopic techniques in order to compare and discuss the spectral results more authoritatively. Hence, Ph$_3$SnL$_1$H.OH$_2$ (1) included.

“isostructural” is used in the wrong context here {p. 65} – the author means same coordination number/geometry {see also p. 77}. It is more precise to mention that the structures of 2 and 3 are isomorphous {p. 71}

Isostructural is correct which means same coordination/ geometry, and hence not changed.

It is not possible to locate H atoms in X-ray crystallography. There can be evidence but as there are no electrons in a bound H atom, only between its nucleus and the atom it is bound to, the position of an H atom can only be inferred. The candidate needs to modify the discussion on p. 73 accordingly.

Agreed with the reviewer’s comment concerning location of H-atom. While solving the structures, H-atoms were placed in the positions indicated by a difference electron density map and their positions were allowed to refine together with individual isotropic thermal parameters. This is a standard practice to
locate H-atoms and the results were also published by us i.e. T.S. Basu Baul, K.S. Singh et al., J. Organomet. Chem., 690 (2005) 4232 (Thesis ref. No. 20) and hence the text is not modified.

It is not acceptable to have the numbering scheme in 3.3.3 and beyond. Structure 1 has already been assigned and so structure 1 on page 78 should be 6, etc.

For convenience of discussion, the chapters are divided into sections and sub-sections. So there is no need to change the compound numbers in the text.

It should be mentioned that the structures of 4 and 5, in 3.3.3, are isomorphous {p. 80}

Isostructural is correct which means same coordination/geometry, and hence not changed.

Throughout the thesis mention is made of “graph set motif” – this must be accompanied by a citation to the literature.

Graph set motif reference is already provided in the text which is Ref. No. 69.

Lorentz should not be italicized on p. 91; see also p. 94 and later in the thesis

Lorentz is italicized in the thesis. Both normal and italics style are correct. We have adopted the chemistry journal style but not the crystallography journal and hence not changed.

The description of the experimental sections in Chapter 3 must be condensed into one cohesive summary.

It appears that the candidate has “cut & paste” from the publications. This is not entirely acceptable. The entire chapter must be selfconsistent and read as such. Aspects of the discussion (numbering scheme) and experimental must be consolidated.

For convenience of discussion of the section i.e. 3.4.5 (X-ray crystallography), has been divided further into sub-sections. i.e.3.4.5.1 (tributyltin), 3.4.5.2 (triphenyltin) and 3.4.5.3 (tribenzyltin). It deals with three different set of samples (i.e. R = Bu, Ph, Bz). Furthermore, the structural refinements were obtained using different programmes. So the mention of the separate experimental details for three different types is necessary in order to have authoritative information and hence not condensed.
CHAPTER 4
Why can not the 13C NMR be recorded for the L7-L10 ligands? What is the meaning of "...complexed ligands, which were generated in situ, are..." {p. 102}

It is clearly mentioned in the text, that the free ligands L7',L10' could not be synthesized owing to the solubility problem of one of the starting materials in water and common organic solvents. (Please refer to section 2.3 synthesis of ligands, p.22). Therefore, 1H & 13C NMR could not be recorded. However, the ligand frame work could be generated during the reaction of R3SnL6H (R = Bu and Ph) with appropriate substituted aniline (complexed ligands) (Refer to Section 2.2, p.22).

The meaning of the sentence beginning "A and p values..." is unclear and needs attention {p. 106}
We feel that the discussion is clear and is also mentioned in a similar way in the publication i.e. T.S.Basu Baul, K.S.Singh, A. Lycka, A. Linden, X. Song, A. Zapata & G. Eng, Appl.Organometal.chem., 20 (2006) 788-797 and hence, not changed.

The word "atomic" occurring between "anisotropic" and "displacement" is unnecessary {p. 115}
Corrected in the thesis, as suggested.

The statement in the box on p. 109 should be included in 4.5.5 without the box. In fact this statement appears a little melodramatic – the most useful criterion for judging a structure is the value of wR(F2) which should be less than 0.200.
The purpose of using the box is to highlight the justification. So it can be seen at a glance and the same justification has also appeared in the publication cited above. Hence, not changed.

CHAPTER 5
Some comments concerning Chapter 5 are to be found above
Corrected as suggested.

The word “but” {p. 151} referring to the benzene solvent molecule is inappropriate.
Corrected as suggested.

CHAPTER 6
It would be useful to indicate the significance of the various values, e.g., are high values desirable?
The low values of the toxicity data are desirable and are clearly mentioned in the text and in the tables 6.1-6.4. The significance of these values are also justified in the text.

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