

## The Mössbauer Isomer Shift of Tin(II) Compounds

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It is the custom of inorganic chemists to distinguish the formal oxidation states tin(IV) and tin(II). In compounds of the latter, tin uses two of its valence electrons to form two bonds with one-electron donors, leaving an electron pair in a singlet ground state. This lone pair is stereochemically active in perturbing the first coordination sphere which adjusts to accommodate its presence, or is chemically active in Lewis base adduct formation with suitable electron pair acceptors.

It has also become customary since it was first pointed out in 1962 [1] for the Mössbauer spectroscopist to distinguish the tin oxidation states by the Sn-119m Mössbauer Isomer Shift (I.S.) parameter [2]: tin(II) > tin metal > tin(IV). The two allotropes of tin metal, the tetrahedral, gray,  $\alpha$ -form (I.S. = 2.10 mm/s vs. SnO<sub>2</sub>) and the tetragonal, white,  $\beta$ -form (I.S. = 2.65 mm/s vs. SnO<sub>2</sub>), both formally tin(0), then fall between tin(II) and tin(IV) [3]. The electron bookkeeping principles embodied in the oxidation state concept are not useful when applied to covalent compounds in which complete electron transfer does not take place. However, the results of diffraction studies on tin(II) compounds show vacant coordination sites presumably occupied by the lone pair, which must, therefore, reside in a hybrid orbital rather than being localized in the pure atomic tin 5s<sup>2</sup> orbital. Among several examples cited in our recent reviews of structural tin chemistry [4], are compounds with coordination numbers (C.N.) at tin of two [ $(h^5-C_5H_5)_2Sn$  (e.d.) [5] and  $h^5-C_5H_5SnCl$  (X-ray) [6]], three [ $SnSO_4$  [7],  $Sn(O_2CH)_3^-$  [8], and  $SnCl_3^-$  [9] (X-ray)], four [ $Sn(S_2COCH_3)_2$ ,  $Sn[S_2CN(C_2H_5)_2]_2$  [11] and  $Sn(O_2C_3HC_6H_5CH_3)_2$  [12] (X-ray)] and six [ $Sn_2EDTA \cdot 2H_2O$  [13],  $Sn(II)Sn(IV)(O_2CC_6H_4NO_2-ortho)_4O \cdot THF$ ] [14] which are, respectively, three-, four-, five- and seven-coordinated, when the lone pair is included. No five-(pseudo-six)coordinated examples are known to us [4]. These compounds and ions exhibit <sup>119m</sup>Sn

Mössbauer I.S. values > tin metal. However, several other classes of compounds which also formally contain tin in its +2 oxidation state have been characterized recently whose I.S. values fall below that of tin metal.

We can identify the following classes of tin(II) compounds:

- (i) tin(II) compounds bound only by electro-negative ligands;
- (ii) adducts of tin(II) compounds with main group Lewis acids which have no non-bonding electrons available in the valence shell;
- (iii) complexes such as those in (ii) in which the tin atom is further coordinated;
- (iv) adducts of tin(II) compounds with transition metal Lewis acids which have non-bonding electrons available in the valence shell;
- (v) complexes such as those in (iv) in which the tin atom is further coordinated;
- (vi) adducts of tin(II) compounds with subvalent main group Lewis acids which have non-bonding electrons available in the valence shell;
- (vii) tin(II) compounds with electropositive ligands.

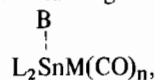
Compounds of category (i) possess a stereochemically active lone pair except when the ligands are severely electronegative as in  $(C_6H_6)Sn(AlCl_4)_2 \cdot C_6H_6$  [C.N. = 7 at tin] [15],  $(C_6H_6)SnCl(AlCl_4)$  [C.N. = 6] [16] and  $(C_6H_5)_3Sn(IV)Sn(II)NO_3$  [C.N. at tin(II) = 5] [17] in which the lone pair is presumably pulled into a tin 5s-orbital. In the many other compounds of this class the C.N. ranges from two-(pseudo-three) to nine-(pseudo-ten) as in tin(II) chloride [18].

Examples of category (ii) species are confined to adducts of bis- $h^5$ -cyclopentadienyltin(II) and its analogues with boron [19, 20] and aluminium [20, 21] trihalides.

There are no authenticated examples of category (iii).

In the dozen or so diamagnetic compounds of category (iv), a three-coordinated tin atom is bonded to a transition metal, principally a group six metal carbonyl residue [22–24]. The structure of  $\{[(CH_3)_3Si]_2CH\}_2SnCr(CO)_5$  is known [24].

The coordination of bases to the tin atom of category (iv) compounds appears to confer additional stability. The diamagnetic complexes of category (v), formulated generally



contain a four-coordinated tin atom bonded to a transition metal carbonyl residue with M = Cr, Mo,

W(n = 5) or Fe(n = 4) [25]. The structure of  $(t\text{-C}_4\text{H}_9)_2\text{SnCr}(\text{CO})_5 \cdot \text{C}_5\text{H}_5\text{N}$  is known [25].

Only a single example, the dimeric, orange solid  $\{[(\text{CH}_3)_3\text{Si}]_2\text{CH}\}_2\text{Sn}\}_2$  [27] for which a structural determination shows a bond between two three-coordinated tin atoms [28], is available to illustrate category (vi) [29].

In category (vii) we again have only a single example,  $[\text{h}^5\text{-C}_5\text{H}_5(\text{CO})_3\text{W}]_2\text{Sn}$ , for which structural information is lacking, but some small degree of association exists in solution which may also be through a tin-tin interaction as above.

The I.S. data for the compounds in the above categories are as follows: (i) and (ii) > tin metal; (iv), (v), (vi) and (vii) < tin metal.

Two mechanisms are available to account for a reduction in I.S. value, electron withdrawal or the shielding of electron density from the tin nucleus by populating non-s atomic orbitals. Both operate in the same direction, but the latter may be effected in two possible ways, by adduct formation which populates the acceptor orbitals at tin, or by populating these orbitals by transition metal non-bonding electrons in a  $\pi$ -interaction taking place along the tin-transition metal axis. Direct comparisons are available for the bis(cyclopentadienyl)tin ligand and its complexes. The parent  $(\text{h}^5\text{-C}_5\text{H}_5)_2\text{Sn}$  [category (i)] [30] and its boron and aluminum trihalide adducts [category (ii)] exhibit the same I.S. values ( $3.8 \pm 0.1$  mm/s) [19, 20]. The complexes with pentacarbonyl group six transition metal residues [22] [category (iv)], on the other hand, have much lower I.S. values ( $1.9 \pm 0.1$  mm/s). In  $(\text{h}^1\text{-R})_2\text{SnFe}(\text{CO})_4 \cdot \text{C}_5\text{H}_5\text{N}$  (R =  $\text{C}_5\text{H}_5$ ,  $\text{C}_5\text{H}_4\text{CH}_3$ ) [22] [category (v)], the I.S. is further lowered to 1.45 mm/s. [31, 32]. The effect on I.S. of adduct formation by transition metal carbonyl moieties appears to be independent of C.N. at tin. Thus the monomeric bis(ketoenolato)tin(II) compounds [33] of category (i) containing four-(pseudo-five)coordinated tin with I.S. = 2.9–3.6 mm/s form complexes  $\text{L}_2\text{SnM}(\text{CO})_n(\text{h}^5\text{-C}_5\text{H}_5)_m$  of category (v) in which M = Cr, Mo and W; n = 5, m = 0; Mn, n = 2, m = 1, with I.S. = 1.7–2.0 mm/s which contain five-coordinated tin.

Taking our observations one by one, adduct formation of the tin(II) lone pair by a main group three Lewis acid results in negligible perturbation of  $|\psi(\text{O})|^2$  at tin [34]. However, adduct formation by a transition metal Lewis acid results in a large degree in I.S. value, and this is accompanied by an equally dramatic increase in Quadrupole Splitting (Q.S.). These changes can be equivalently rationalized by electron withdrawal or by the more conventional synergistic  $\sigma$ -plus  $\pi$ -interaction with the transition metal. The tin atoms in these category (iv) species would be expected to exhibit Lewis acid character, which would account for the stability of the complexes cited as examples of category (v). The I.S. of

these latter complexes is reduced by shielding brought about by the solvation of the tin by base molecules. The bonding of the dimer which constitutes category (vi) has been described in terms of a mutual  $2 \times 2$ -electron, bent donor-acceptor interaction between two  $\text{R}_2\text{Sn}$ : monomers [28]. Vacant non-s orbitals on the tin are thereby populated, decreasing  $|\psi(\text{O})|^2$  by shielding. Electron release to tin in the monomeric tungsten carbonyl derivative [22] in category (vii) would tend to give the lone pair predominantly 5p-character [35] and shield the tin nucleus, reducing effective  $|\psi(\text{O})|^2$ , reducing the I.S. This is the opposite of the case cited in category (i) in which severely electronegative ligands result in a largely 5s-lone pair, and increase  $|\psi(\text{O})|^2$  and the I.S. [36].

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### References and Notes

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- 31 The comparison drawn between the category (iv) and (v) examples is not strictly direct. The former adducts contain group six metal pentacarbonyls, while the latter contain iron tetracarbonyl. However, the effect of changing the transition metal carbonyl residue can be evaluated from the data for the pyridine and DMSO complexes of  $(t\text{-C}_4\text{H}_9)_2\text{SnM}(\text{CO})_n$  in which M = Fe, n = 4; M = Cr, n = 5; the iron derivatives have lower I.S. values by 0.1–0.2 mm/s [25(c)].
- 32 Unlike the bis(cyclopentadienyl)tin derivatives of categories (i), (ii) and (iv) in which  $h^5$ -cyclopentadienyl groups are present [refs. 5 and 6; P. G. Harrison and M. A. Healy, *J. Organometal. Chem.*, 51, 153 (1973)], the two pyridine complexes of category (v) contain  $h^1$ -cyclopentadienyl groups [22].
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- 34 This can be interpreted in terms of either negligible electron drift away from tin toward boron or aluminum, or extensive mutually compensating effects.
- 35 The opening of the  $\langle\text{W-Sn-W}\rangle$  by the steric bulk of the tungsten moiety would have the same effect.
- 36 Possible association to a tin-tin bonded dimer in the solid state would give rise to a reduced I.S. from shielding by the populated non-s orbitals.