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# Colored and Colorless Tin(II) Amines

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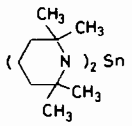
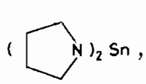
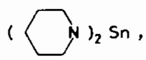
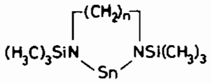
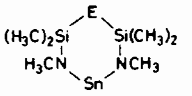
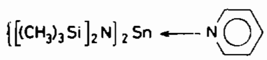
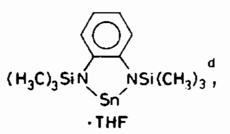
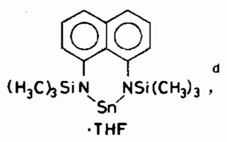
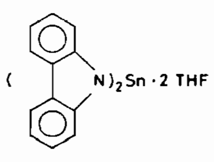
The results of recent experiments allow a new understanding to be reached concerning the origin of the intense red colors exhibited by certain compounds of the formula $(R_2N)_2Sn(II)$. These strong colors arise despite there being no apparent chromophore, and are thought to be associated with thermally accessible neighboring electronic singlet states consistent with the diamagnetism, absence of esr signals and reversible thermochromic behavior observed [1]. We present in this Letter a view which rests upon the following observations: (i) the colored derivatives are monomeric while the colorless derivatives show evidence of association or are obviously chelated; (ii) whether the species will be monomeric or associated is a sensitive function of the steric requirements of the substituents at nitrogen; (iii) where direct comparisons can be drawn, the colorless compounds are qualitatively more stable to hydrolysis and oxidation than their intensely colored analogues; and (iv) the tin-119m Mössbauer Isomer Shift (I.S.) and Quadrupole Splitting (Q.S.) values for the highly colored derivatives are larger (I.S. = 2.9–3.1; Q.S. = 2.4–3.5 mm/s) than for the analogous, simple colorless compounds (2.6–2.7 and 2.1–2.5 mm/s, respectively); however the chelated derivatives and those with active donor atoms not directly connected to tin exhibit equally high I.S. (2.8–3.5 mm/s), but much lower Q.S. (1.2–2.4 mm/s) values [see Table I].

The tin(II)–nitrogen bond was first formed in 1936 in the chelated phthalocyaninatotin(II) [2]. Subsequently, it was shown that tin(II) alkoxides add to the multiple bonds of isocyanates to form adducts which by analogy with previous work were assigned the tin(II)–nitrogen, SnN(R)C(=O)OR, rather than the SnOC(=NR)OR structure [3]. However, the evidence for this formulation is not unequivocal, and the alternative structure cannot be ruled out [4]. Activated amines such as imidazole and di- and triazoles liberate cyclopentadiene from bis($h^5$-cyclopentadienyl)tin(II) to form tin(II)–nitrogen derivatives [5] whose structure can be unequivocally assigned; however, like the compounds above,

TABLE I. $^{119m}$Sn Mössbauer Parameters[a].

| | IS[b] | QS[c] |
|---|---|---|
| *Highly Colored $(R_2N)_2Sn(II)$* | | |
| $\{[(CH_3)_3Si]_2N\}_2Sn$,[d] *1* | 2.88 | 3.52 |
| $[(C_6H_5)_2N]_2Sn$ | 3.09 | 2.55 |
| $[(CH_3)_3SiNC_6H_4CH_3$-<u>para</u>$]_2Sn$ | 2.95 | 2.4 |
|  | 2.92 | 2.76 |
| *Colorless $(R_2N)_2Sn(II)$* | | |
| $[(CH_3)_2N]_2Sn$[e] | 2.72 | 2.07 |
| $(\lceil N)_2Sn$[f] | 2.72 | 2.03 |
|  , 6 | 2.58 | 2.18 |
|  , 7 | 2.63 | 2.12 |
|  n = 2[d] | 2.66 | 2.50 |
| 3[d] | 2.71 | 2.34 |
| 4[d] <br> 4 | 2.67 | 2.24 |
|  E = $CH_2$ | 2.69 | 2.26 |
| E = O | 2.65 | 2.09 |
| *Tin(II) Amines Complexed by Base* | | |
|  | 2.77 | 2.78 |
|  , 2 | 2.67 | 2.85 |
|  , 3 | 2.70 | 2.31 |
|  | 2.94 | 2.70 |

*(continued on next page)*

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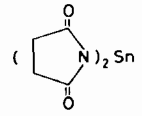
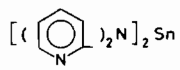
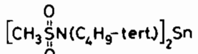
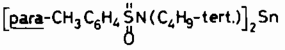
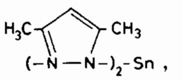
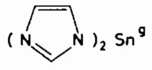
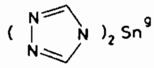
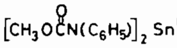
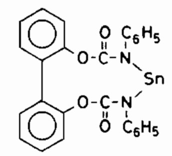
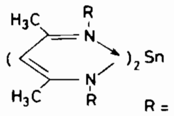
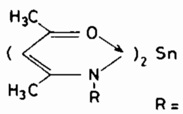
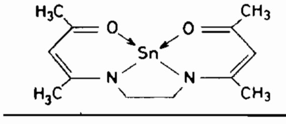
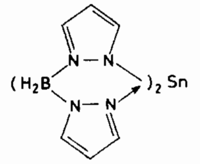
TABLE I. *(Continued)*

| | | |
|---|---|---|
| *Tin(II) Amines with Active Donor Atoms Not Directly Bound to Tin* | | |
|  | 3.11 | 2.08 |
|  | 2.83 | 2.40 |
|  $[CH_3\overset{O}{\underset{O}{S}}N(C_4H_9\text{-tert})]_2Sn$ | 3.14 | 1.99 |
|  $[para\text{-}CH_3C_6H_4\overset{O}{\underset{O}{S}}N(C_4H_9\text{-tert.})]_2Sn$ | 3.22 | 2.03 |
|  13 | 2.99 | 1.99 |
|  [g] | 3.09 | 2.02 |
|  [g] | 3.60 | 2.14 |
|  $[CH_3O\overset{O}{C}N(C_6H_5)]_2Sn$[h] | 3.11 | 1.88 |
|  | 3.46 | 1.56 |
| *Chelated Tin(II) Amines* | | |
|  9 | | |
| R = $C_6H_5$ | 2.89 | 1.87 |
| para-$CH_3C_6H_4$ | 2.95 | 1.76 |
| F | 3.0 | 1.9 |
|  10<br>R = para-$CH_3C_6H_4$ | 2.92 | 1.82 |
|  11 | 2.85 | 1.69 |
|  12 | 3.18 | 1.76 |
| PcSn[j] | 2.83 | 1.47 |
| (meso-tetraphenylporphyrinato)$_2$Sn | 2.92 | 1.24 |

[a] Recorded at 77 K *vs.* a Ca $^{119m}SnO_3$ source (New England Nucl. Corp.) by published techniques [30].
[b] ±0.06 mm/s.
[c] ±0.12 mm/s.
[d] Ref. 10.
[e] Reported as 2.80 and 3.17 ± mm/s, respectively in ref. [7].
[f] At ambient temperatures, 2.60 and 2.13 mm/s, respectively.
[g] Ref. 5.
[h] Ref. 3c.
[i] Ref. 3b.
[j] Recorded as 2.96 and 1.43 in ref. [2c] and as 2.78 and 1.40 mm/s in ref. [31].

these white solids are associated through a second atom in the ligand [6].

More recently, two tin(II) amines were synthesized by the lithioamination of tin(II) chloride, the white solid bis(dimethylamino)tin(II) which is dimeric in cyclohexane [7], partially associated in the gas phase (by electron diffraction) [8], and exhibits changes in its nmr spectrum on cooling [7]; and the orange-yellow solid bis[N,N-bis(trimethylsilyl)amino] tin(II), *1*, which melts at 37–38 °C [9] to an intense red, distillable liquid (bp 109–110 °C, 0.75 torr) [10] and is monomeric in cyclohexane [9, 11, 12]. The closely-related derivatives $[(R_3E)_2N]_2Sn$, in which R = $CH_3$ and $C_2H_5$, and E = Si and Ge, and $\{[(C_6H_5)_3Ge]_2N\}_2Sn$ are also reported to be highly colored and monomeric [12].

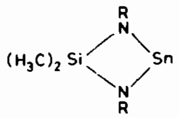
It is becoming recognized that organotin compounds are acutely sensitive to the steric requirements of substituent groups, changing their structure [13], the coordination number at tin, molecularity and chemical reactivity with the size of the attached ligands. All organotin(IV) amines, for example, in which the only nitrogen atom in the molecule is bonded to tin are monomeric [14], and all those derivatives containing trialkyltin groups are liquids at ambient temperatures. But N-trimethyltin aziridine in which the nitrogenous ligand has exceptionally small bulk is a solid whose enhanced Q.S. (2.24 mm/s) value suggests a higher coordination number at tin. Even such closely-related derivatives as the azetidine and 2-methylaziridine are monomeric liquids with much lower Q.S. values (1.35 and 1.43 mm/s, respectively). In addition, the dimethylamino derivative (Q.S. = 0.81 mm/s), which melts over 100 °C lower than its aziridine analogue, fumes in moist air, while the nitrogen-bridged aziridine is moderately stable to hydrolysis [15] Analogously, the one-dimensional, nitrogen-bridged structure of trimethyltin glycinate

[16] rearranges to the more conventional carboxylate-bridging in the more bulky tricyclohexyl derivative [17], and X-ray crystal structure determinations show that while $(\text{tert.-}C_4H_9)_2SnCr(CO)_5 \cdot NC_5H_5$ requires its molecule of base to be bonded to the tin atom for stability [18, 19], the stable compound $\{[(CH_3)_3Si]_2CH\}_2SnCr(CO)_5$ contains tin in the three-coordinated form [20, 21].

We have synthesized several series of compounds which serve to define the crossover point between the limiting structures for the tin(II) amine derivatives. For example, incorporating the $(CH_3)_3Si{-}\overset{|}{N}{-}Sn{-}\overset{|}{N}{-}Si{-}(CH_3)_3$ unit present in *1* into a five- or six-membered aromatic carbocycle gives rise to yellow solids which are stable 1:1 adducts of the THF solvent medium used in their syntheses, as *2* (mp 88 °C dec) [10] and *3* (82.5 °C) [10]. The corresponding aliphatic heterocycles *4*, n = 2 (134–5 °C), 3 (108–9 °C) and 4 (83.5–84.5 °C) [10] and *5*, E = $CH_2$ (169 °C) and E = O (167 °C) prepared by lithioamination are white compounds formed free of solvent [22]. Low temperature nmr spectra of *5* [E = $CH_2$: $T_c$ = 304 K, $\Delta G^{\neq}$ = 16.1 kcal/mol; E = O: 283 K; 14.9 kcal/mol] contain two resonances for the $N\text{-}CH_3$ and four for the $Si(CH_3)_2$ protons, specifying pairwise bridging of nitrogen atoms in a four-membered $Sn_2N_2$ ring. Cyclic aliphatic amines likewise give white solid derivatives which exhibit low temperature nmr spectra in which bridging and terminal amine groups in the dimer can be distinguished [pyrrolidine, *6*: $T_c$ = 298 K; $\Delta G^{\neq}$ = 14.4 kcal/mol; piperidine, *7*: 353 K; 17.8 kcal/mol] [23]. Tin(II) diaziridine (205 °C decomp) is an infusible, sparingly soluble, white solid which exhibits a tin-119m Mössbauer resonance at ambient temperatures, reflecting its associated nature [24, 25]. The carbazole derivative prepared by transamination from bis(dimethylamino)tin(II) forms a white 2:1 adduct with THF (mp 184–185.5 °C), while the related pyrrole derivative could not be isolated.

Compounds in the series $\{[(CH_3)_3Si]_2N\}_2Sn$ [9, 10], $[(CH_3)_3SiNC_6H_4CH_3\text{-}para]_2Sn$, (soft solid) and $[(C_6H_5)_2N]_2Sn$ (mp 120–121 °C) are intensely red colored, while the derivatives of the aliphatic cyclic amines [10] and dimethylamine [7] are colorless. Bis(diisopropylamino)tin(II), on the other hand, is intensely colored [26]. Although the bis-piperidine derivative is colorless, the 2,2,6,6,-tetramethyl derivative (mp 35 °C) is intensely red colored. Thus it appears that the steric requirements which arise from branching at the carbon α- to the nitrogen atom result in intense red colors in the tin(II) derivatives, presumably because association through N→Sn(II) bridging or the formation of solvates is then blocked.

Corroboration for these views comes from the recent work of Veith who has prepared the four-membered, 1,3-dialkyl-2,2-dimethyl-1,3,2,4$\lambda^2$-diazasilastannetidine heterocycles [27], *8*:



The R = $C_4H_9$-tert. derivative is a red colored liquid, monomeric in benzene, and X-ray diffraction shows the presence of monomers in the orange solid, while the R = $C_3H_7$-iso derivative is white and dimeric in solution and in the solid state [28].

Phthalocyaninatotin(II) is reported to be a blue-black, crystalline solid [2]. We have prepared the equally infusible *meso*-tetraphenylporphyrin derivative by transamination from bis(dimethylamino)tin(II), and it has an intense dark green color. Apparently, in this case the intense colors arise from the Soret band in the ligand. Other higher coordinated tin(II)–nitrogen systems derive from chelating ligands, such as the nitrogenous acac derivatives, the 2-phenylamino-4-phenylimino-2-pentenes, *9*, where R = H (mp 191–2 °C) and $CH_3$ (208–9 °C), bis(N-*para*-tolyl-4-aminopent-3-en-2-ono), *10* (79–81 °C), bis(acetylacetone)ethylenediimino, *11*, (117–9 °C) and bis(di-1-pyrazolylborato)tin(II), *12* (130 °C) prepared by transamination from bis(dimethylamino)tin(II), and are only lightly yellow colored or white. These complexes are monomeric (the crystal structure of phthalocyaninatotin(II) is known [2c]). Bis(3,5-dimethylpyrazolato)tin(II), *13*, (280 °C with decomp.) is a white, insoluble, one-dimensional polymer prepared by transamination of bis(dimethylamino)tin(II). The analogous 3,4,5-trimethylpyrazole and 1,2,4-triazole derivatives are known [5].

Bis(di-tert.-butyl)phosphinotin(II) is a kinetically-stable dimer which is strongly red colored [29]. Apparently, the systematics of the tin(II) phosphine derivatives are different.

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11 Recognition of the monomeric character of [N,N-bis-(trimethylsilyl)amino] tin(II) represents a revision of our earlier view [10] which was based upon osmometric molecular weight data recorded by commercial laboratories and mass spectral data recorded by a departmental service. Precautions in both cases were insufficient to prevent hydrolysis and/or oxidation of this sensitive species.

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21 The analogous germanio-complex is likewise stable without the assistance of base coordination [M. F. Lappert, S. J. Miles, P. P. Power, A. J. Carty and M. J. Taylor, *Chem. Commun.*, 458 (1977)].

22 We are grateful to Professor H. Bürger of the Gesamthochschule, Wuppertal, Germany for the gift of the bis-(N-methylaminodimethylsilyl)methane and other ligands.

23 The corresponding values for [(CH$_3$)$_2$N]$_2$Sn are $T_c$ = 253 K; $\Delta G^{\neq}$ = 12.5 kcal/m [7].

24 J. J. Zuckerman, *Advan. Organometal. Chem.*, *9*, 21 (1970).

25 The observation of ambient-temperature tin-119m Mössbauer spectra for certain monomeric molecular solids [G. M. Bancroft, K. D. Butler and T. K. Sham, *J. Chem. Soc. Dalton Trans.*, 1483 (1975)] does not affect our conclusion which is based upon close-analogy with the trimethyltin(IV) aziridine and other tin(II) and tin(IV) amines [15].

26 This compound could not be isolated; [(CH$_3$)$_3$SiNCH(CH$_3$)$_2$]$_2$Sn has been reported as a brown oil [12].

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