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Organotin(IV) Chalcogenides as Ligands

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Recent reports on the isolation of metal complexes of di-n-butyltin oxide (*I*; dbto) and μ-oxo-bis-(tri-n-butyltin) (*II*; otbt) [1–5], prompt us to publish on a number of synthetic approaches we used in the past in attempts at isolating metal complexes with otbt and a number of organotin(IV) sulfides, *i.e.*, di-n-butyltin sulfide (*III*; dbts) and μ-thio-bis(tri-n-butyltin) (*IV*; ttbt). This experimental work was initiated following a research proposal by one of us (CMM) [6].

$[(n\text{-}C_4H_9)_2SnO]_x$ (*I*)

$[(n\text{-}C_4H_9)_3Sn]_2O$ (*II*)

$[(n\text{-}C_4H_9)_2SnS]_x$ (*III*)

$[(n\text{-}C_4H_9)_3Sn]_2S$ (*IV*)

Our earliest work in this direction involved attempts at isolating metal complexes of ligands *II–IV* by reacting these ligands with hydrated 3d metal perchlorate solutions in triethyl orthoformate (teof), at temperatures ranging between 40–60 °C. Addition of the ligand in various metal to ligand ratios (ranging from as high as 2:1 to as low as 1:6) to the metal salt solution undoubtedly resulted in complexation, as evidenced by the immediate change of the color of the solution to a bright brown with a reddish or greenish tint (depending on the metal ion present). However, continuation of stirring at 40–60 °C invariably resulted in the precipitation of small amounts of khaki to beige solids of uncertain nature. The complexes initially formed in solution presumably decomposed at the reaction temperature [5].

During subsequent work, the ligand was added at room temperature to the metal perchlorate solution in teof, absolute ethanol or *p*-dioxane, while all operations were being performed in a dry nitrogen atmosphere. Again, complex formation was indicated by dramatic color changes upon addition of the ligand. The reaction mixture was stirred for a few hours at ambient temperature, and then allowed to stand at 0 °C for several days. In most cases, the solutions maintained their bright colors, but yielded no precipitates. Nevertheless, in a few occasions ($M = Cr^{3+}$, L = otbt; $M = Mn^{2+}$, L = dbts; $M = Fe^{3+}$, L = ttbt; $M = Co^{2+}, Ni^{2+}$, L = otbt, dbts; $M = Cu^{2+}$, L = dbts, ttbt), well-defined solid complexes of the $ML_n(ClO_4)_m \cdot xL'$ ($n = 0.5–2$; $m = 2$ or 3; L = otbt. dbts, ttbt; L′ = ethanol or *p*-dioxane) type gradually precipitated in low yields (5–10% of the theoretical). The IR spectra of these complexes include bands characteristic of coordinated ethanol (ν_{OH}) [7] or *p*-dioxane (ν_{C-O-C}) [8], as well as exclusively ionic ClO_4^- (single ν_3 and $\nu_4(ClO_4)$ bands) [9]; as far as coordination of the organotin ligands is concerned, band attributable to $\nu_{Sn-O-Sn}$, as or $\nu_{Sn-S-Sn}$, as are observed at 740–710 [1–5] or 390–370 [10, 11] cm^{-1}, respectively, in the spectra of the solid metal complexes. These data favor coordination of the ligands through oxygen or sulfur; they also suggest that the oligomeric dbts [12] does not depolymerize to $(n\text{-}C_4H_9)_2Sn{=}S$ prior to coordination, but coordinates as an oligomeric ligand. Tentative ν_{M-O} and ν_{M-S} (metal–organotin ligand stretching modes) band assignments were: ν_{M-O} range between 466 for Cr^{3+} and 410–395 cm^{-1} for M^{2+} complexes [5, 8, 13]; ν_{M-S} range between 338 for Fe^{3+} and 315–290 cm^{-1} for M^{2+} complexes [8, 14, 15]. It should be noted that complexes containing coordinated ethanol were precipitated not only when absolute ethanol was used as the reaction medium, but also when the preparation was made in teof; the latter compound is hydrolyzed to ethanol and ethyl formate while dehydrating metal salts [16].

The research herein reported further substantiates the results of Narula *et al.* [1–5], and demonstrates that a wide variety of organotin(IV) oxide or sulfide metal complexes can exist. The ligands of interest are certainly sufficiently basic to readily function as electron-pair donors toward metal ions [17–19]. The only impediments to the isolation of their metal complexes are the lack of developed synthetic procedures and the temperature-sensitivity of these complexes. We are planning to initiate synthetic studies aimed at the preparation of the whole series of 3d metal perchlorate complexes with ligands *I–IV*, by employing preparative methods involving significantly milder interaction conditions (*i.e.*, as mild or milder than the conditions used by Narula *et al.* [1–5]), relative to the synthetic methods employed during the work herein reported.

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