Synthesis of the First Hydroxomonoaryltin(IV) Complexes. Crystal and Molecular Structure of [{Sn[C₆H₃(N=NC₆H₄-Me-4')]₂,Me-5}Cl₂(μ-OH)]₂ †

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Supplementary data available: further details of the structure determination (complete bond lengths and angles, H-atom coordinates, structure factors, thermal parameters) have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, Germany. Any request for this material should quote a full literature citation and the reference number CSD W-3300.

Results and Discussion

Synthesis.—Tin(II) chloride reacts in refluxing xylene with [HgCl₂] (L = C₆H₅(N=NC₆H₄-R-4')₂, R = Me or MeO) to give metallic mercury and [SnL₂Cl₂] (L = mpap or mopap). Complex 1 reacts with Cl⁻, dimethyl sulfoxide or [Hg(dmap)₂] (dmap = C₆H₃(CH₂)₃NMe₂) to give, respectively, [Sn(mpap)Cl₂] 3, [Sn(mpap)Cl₂(OSMe₂)] 4 or [Sn(mpap)(dmap)Cl₂] 5. Several types of hydrolytic process occur when 1, 2 or [Sn(mpap)Ph₂Cl] react with various ligands. Thus, [Hg(dmap)Cl₂] reacts with 1 or 2 as a base to give [{SnLCl₂(μ-OH)}₂] (L = mpap 6 or mopap 7) and Hg(HdmapiCl₂). Similarly, Ph₃CNMe₂ (bdma) reacts with 1 (1:1) to give the hydrolysis product [Hbdma][Sn(mpap)Cl₂(OH)] 8. By treating 6 with excess of NaBr, [{Sn(mpap)Br₂(μ-OH)}₂] 9 can be obtained. Acetic anhydride reacts with complex 6 to give [Sn(mpap)Cl₂(O₂CMe)] 10, but not with 8. The complex [Sn(mpap)Ph₂Cl] reacts with Tl(acac) (acac = acetylacetonate), NaH or Ag₂O to give the hydrolysis product [Sn(mpap)Ph₂(OH)] 11. The crystal structure of 6 was determined at -95 °C; the dimeric doubly bridged nature of the compound was confirmed. The Sn-O bridges are asymmetric, the bond lengths depending on the nature of the trans ligand. Two molecules of diethyl ether form hydrogen bonds to the bridging OH groups; another diethyl ether molecule is disordered over a symmetry centre. The structure of compound 7 was also determined; it too is dimeric with two hydroxido bridges, but the refinement was unsatisfactory, probably because of twinning effects.

Whereas the hydrolysis of halogenoorganotin(IV) complexes to hydroxo-, oxo- and oxohydroxo-organotin(IV) complexes is well known, processes of hydroxomonoaryltin(IV) complexes are very rare because they are usually in equilibrium with the corresponding oxo-derivatives and water.† As far as we are aware, only a few such complexes have been studied by X-ray diffraction, viz. [{SnMe₂(OH)}₂] 2, [{SnPh₂(OH)}₂], [{SnCl₂(H₂O)(μ-OH)}₂] (R = Et or Bu) and [{SnBu₂X₂(μ-OH)}₄] (X = F, Cl or Br). A complex [{Sn₃(μ-OH)}₄] 12 has been reported. We are currently investigating the synthesis of aryltin(IV) complexes as a part of a wider project involving the use of organomercury compounds as transmetallating agents. In particular, we have developed several methods of synthesising (phenylazo)phenyltin(IV) complexes.⁸

In this paper we report the synthesis of some derivatives of [SnLCl₂] and [SnPh₂Cl₂], where L is a p-Me- or p-OMe-substituted 2-(phenylazo)phenyl chelating ligand. Some of these derivatives are the first hydroxomonoaryltin(IV) complexes reported.† We also report the crystal structure of one of these derivatives, and a partial crystal structure determination of another.

Results and Discussion

Synthesis.—Tin(II) chloride reacts in refluxing xylene with [HgCl₂] (L = C₆H₅(N=NC₆H₄-R-4')₂, R = Me or MeO) to give metallic mercury and [SnL₂Cl₂] (L = mpap 1 or mopap 2) (see formula diagram and Scheme 1). Complex 1 reacts with NMe₂Cl or dimethyl sulfoxide to give [{NMe₂Cl₂Sn(mpap)Cl₂}] 3 or [{Sn(mpap)Cl₄(OMe₂)}₂] 4, respectively. A second aryl group can be transmetallated from mercury to tin by treating [Hg(dmap)Cl₂] (dmap = C₆H₃(CH₂)₃NMe₂) with 1 to give the mixed-ligand complex [{Sn(mpap)-dmap}Cl₂] 5. We have previously used analogous methods to prepare complexes [SnL(Ph₂Cl₂)] and [SnLPh₂Cl₂] (L = C₆H₅N=NPh₂ or mopap).⁶

Complex 1 is stable to atmospheric moisture in solution and in the solid state. It also resists 10 h of refluxing in an acetonewater mixture. However, treatment with various ligands (except for the three mentioned above) led to the formation of hydroxo-complexes. Even the mercurial reagent [Hg(dmap)Cl₂] reacts with 1 or 2 as a base, removing a proton from water and substituting Cl by OH to give [{SnLCl₂(μ-OH)}₂] (L = mpap 6 or mopap 7), instead of transmetallating the aryl group. The
by-product of this reaction is the unusual protonated organomercurial, Hg(Hdmap)Cl₂, which precipitates from the acetone solution; it can also be obtained by treating Hg(dmap)Cl with HCl. The basic character shown by the dmap ligand in Hg(dmap)Cl₂ is also observed in the non-metallated precursor amine PhCH₂NMe₂ (bdma), which reacts with [Hbdrna][Sn(mpap)Cl₃(OH)] to give the cationic complexes [Sn(mpap)Ph₂L′]⁺. Addition of excess of NaBr to complex 6 gives [[Sn(mpap)-Br₂]₂(OH)]⁺. Complex 6 reacts with acetic anhydride to give [Sn(mpap)Cl₂(O₁,C₃Me)] (X = ClO₄), whereas 8 does not react. The complex [Sn(mpap)Ph₂Cl] does not react with 1,10-phenantrone (phen-H₂O), 2,2'-bipyridine (bipy), pyridine (py) or PPh₃ in an attempt to prepare cationic derivatives with such ligands, [Sn(mpap)Ph₂Cl] was treated with AgClO₄. After removing AgCl, addition of the above ligands (L') (1:1) gave mixtures which seemed to contain the expected complexes, [Sn(mpap)Ph₂L']ClO₄, along with some hydrolysis products (such as [Sn(mpap)Ph₂(OH)]Cl₂) that could not be separated. When the reaction with phen-H₂O was carried out in 1:2 molar ratio (Sn:phen), the complex [Sn(mpap)Ph₂(OH)]ClO₄ (X = ClO₄) was obtained along with [Hphen]ClO₄ and some excess of phen-H₂O. We interpret these results (see Scheme 3) assuming that the complex [Sn(mpap)Ph₂(H₂O)]ClO₄, formed first in solution, reacts with the added ligand and with water (adventitious or added with the ligand in the case of phen-H₂O) giving the cationic complexes [Sn(mpap)Ph₂L']ClO₄. The aqua-complex, L' = H₂O, is an acid, the dissociation equilibrium of which can be shifted by the added (basic) ligand to give 11. Upon addition of a second mole of phen-H₂O, not only is this last equilibrium displaced forming 11, but the simultaneous addition of 1 mol of water also shifts the equilibrium system [Sn(mpap)Ph₂(OH)]⁻/[[Sn(mpap)Ph₂-OH] Springer - Journal of Chemical Society, Dalton Transactions (1992) 1840 - J. CHEM. SOC. DALTON TRANS. 1992 - Structure and Spectroscopic Properties of Complexes 1–11. — Repeated attempts to grow crystals of complexes 1–11 were, except for 6 and 7 (see below), unsuccessful. Our proposals of six-co-ordination for complexes 3–5, 8 and 10 and five-co-ordination for 1, 2 and 11 (see Scheme 1) are thus based on solution data and previous reports of similar complexes. Complexes related to 1 and 2, such as [Sn₃C₆H₃(CPh)=NMe]Cl₃, or [Sn₃C₆H₃(CO)₃OPh]Cl₃, have trigonal-bipyramidal structures with axial nitrogen or oxygen atoms, respectively. Complexes 1 and 2 should adopt the same type of structure because the small bite of the 2-(phenylazo)phenyl ligand (ca. 70°) requires its location in a vertical plane and the more electronegative donor atom N should be axial. Whereas the anionic complex 3 behaves in nitromethane solutions as a 1:1 electrolyte, with B = 247 Ω⁻¹ cm² mol⁻¹ in the Onsager equation (Δ = Δ – Δ) in the range 2 × 10⁻² to 10⁻⁴ mol dm⁻³, complex 8 shows an anomalous negative value.
$B = -49 \text{ cm}^{-1}$ in the same range. The $^{1}$H NMR spectrum of 8 in chloroform changes with concentration. With increased concentration the NH signal at $\delta \approx 9.5$ shifts to high field ($\delta \approx 9.3$) and the CH$_{2}$ and Me singlets (at $\delta \approx 2.8$) change to an apparent doublet (at $\delta \approx 2.3$) which should be an AB system and two singlets (at $\delta \approx 2.8$ and 2.9) change to an apparent doublet (at $\delta \approx 2.8$) and two singlets (at $\delta \approx 2.8$). All these data point to the formation of a hydrogen bond RNH...O(H)M when the concentration rises, which could be responsible for the non-ideal electrolyte behaviour of 8.

Complex 5 is assumed to be octahedral by analogy to the related [Sn(mpap)$_{2}$Cl$_{2}$] and [Sn(dmap)$_{2}$Cl$_{2}$] in all reported structures of organotin(rv) complexes containing potential C,N ligands. An N-Sn bond is indeed observed. Furthermore, the IR spectrum of 5 gives bands assignable to v(SnCl) modes at 300 and 280 cm$^{-1}$, cf: [Sn(dmap)$_{2}$Cl$_{2}$] at 320 and 295 cm$^{-1}$.

Crystall Structures of Complexes 6 and 7.—Initially, single crystals of compound 7 were studied. The structure was established as a doubly bridged dimer with crystallographic two-fold symmetry (Fig. 1), but problems with the refinement (see Experimental section) rendered the structure unsatisfactory; the H atoms were not located and estimated standard deviations (e.s.d.s) were high. Furthermore, a region of electron density identified as a diethyl ether molecule (giving a ratio Sn:ether = 1:1) could not be successfully refined. We prefer not to discuss quantitative aspects of this structure.

The structure of complex 6 presented no such difficulties. It too consists of dimers with two bridging OH groups (see Fig. 2) leading to a distorted octahedral co-ordination for both tin atoms. Diethyl ether of solvation is also observed (Sn:ether = 4:5). The Sn$_{2}$OH bridges are asymmetric, with Sn-O bonds trans to the chloro ligands longer [2.193(3), 2.188(3) Å] than those trans to the phenyl groups [2.027(3), 2.015(3) Å]. In octahedral complexes containing the Sn(p-OH)$_{2}$Sn moiety the bridge is symmetric if the other ligands in the Sn,O, plane are identical or similar. These Sn-O bond lengths lie in the range 2.09-2.04 Å when chloro ligands are trans to the OH groups. However, where the ligands are different, as in 6, the bridge is asymmetric. Thus, in [SnCl$_{2}$(H$_{2}$O)(OH)$_{2}$]$_{2}$ (R = Et$^{+}$ or...
Bu

the Sn-O bonds trans to chloro ligands [2.153, 2.169 Å], respectively] are longer than those to ethyl [2.067(3) Å] or butyl [2.047(4) Å] groups. In the current structure the Sn-Cl bonds trans to 2,3-dichloro(2,4) are shorter than those to oxygen [2.402(2), 2.401(2) Å]. The Sn-N bond distances [2.463(4), 2.474(4) Å] are shorter than those in the octahedral complex [Sn(mpap)Cl, 2.58(2), 2.51(2) Å].

The narrowing of the O-Sn-O angles to ca. 70° in the four-membered rings may be regarded as reducing the metal-metal repulsion (Sn-...Sn 3.429 Å); additionally, the electronegativity of the oxygen atoms decreases the repulsion of the Sn-O bonding pairs [valence shell electron pair repulsion (VSEPR) model]. The narrow C-Sn-N angles (ca. 72°) are probably attributable to the chelating nature of the ligand mpap. Other bond angles are correspondingly widened by 10–15° from the ideal 90°.

Two molecules of diethyl ether are involved in hydrogen bonds, each to one OH group. This type of interaction is a common feature in hydroxotin(iv) complexes. The distances O(1)...O(3) 2.64 and O(2)...O(4) 2.68 Å imply strong hydrogen bonds (cf. O-...O 2.59–2.79 in various hydrogen-bonded systems in ref. 14). One further molecule of diethyl ether is disordered over a centre of symmetry and is not involved in hydrogen-bonding interactions.

**Experimental**

The IR spectra, the C, H and N analyses, conductance measurements, melting-point determinations, and NMR spectra were recorded as described elsewhere. Some spectra were recorded on a Varian Unity-300 spectrometer. The NMR spectra of 6, 7 and 15 were measured in (CD,COCD,CO), those of all other complexes in CDCl, with SiMe as use reference. The atom numbering for the 1H and 13C NMR assignments corresponds to the mpap ligand co-ordinated to Sn(1) in Fig. 2.

[Sn(mpap)Cl, 1].—To a suspension of anhydrous SnCl, (500 mg, 2.64 mmol) in xylene (15 cm

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[Sn(mpap)Cl]₂ — To a solution of anhydrous SnCl₂ (250 mg, 1.32 mmol) in xylene (20 cm³) was added [Hg(mpap)Cl] (629 mg, 1.32 mmol); the solution was stirred at room temperature for 12 h and then evaporated to dryness. The residue was refluxed for 5 h. The hot suspension was filtered off over MgSO₄ to remove Hg, the solution concentrated to 1 cm³ and hexane (20 cm³) added to precipitate complex 2 as a red solid, which was treated with an excess of dimethyl sulfoxide and stirred at room temperature for 4 h a new suspension was obtained. After filtration, the resulting suspension was stirred at room temperature for 18 h and then filtered to give complex 3 as a yellow solid. Yield 80%, m.p. 293 °C. v(SnCl) 310, 275 and 250 cm⁻¹. 6(¹H) 8.16 [d, 2 H, H₂H₂], 7.84 [d, 1 H, H₁H₁] = 8.4 Hz, 7.64 [d, 1 H, H₁H₁], J(H₁H₁) = 3 Hz]. 2.76 (m, 1 H, H₁H₁), 2.73 (2 H, H₂H₂) = 8 Hz. 2.40 (s, 3 H, Me), 2.35 (s, 3 H, Me) (Found: C, 35.8; H, 2.8; N, 5.5. C₂₈H₂₈Cl₃N₂O₂Sn requires C, 35.8; H, 2.8; N, 5.5). v(OH) 3410 cm⁻¹. 6(¹H) 8.22-7.25 (m, 7 H, Ph), 2.56 (s, 3 H, Me) and 2.44 (s, 3 H, Me) (Found: C, 40.4; H, 3.5; N, 6.4. C₂₃H₂₈Cl₂NO₂Sn requires C, 40.4; H, 3.4; N, 6.7%).

[Sn(mpap)Cl₂(OH)]⁻ — To a solution of complex 1 (200 mg, 0.46 mmol) in acetone (15 cm³) was added NMe₂Cl (50.5 mg, 0.46 mmol). The resulting suspension was stirred at room temperature for 4 h a new suspension was obtained. After filtration, complex 4 was obtained as a yellow solid. Yield 82%, m.p. 180 °C. v(νOH) 3470 cm⁻¹. 6(¹H) 8.00-7.12 (m, 7 H, Ph), 2.56 (s, 3 H, Me) and 2.44 (s, 3 H, Me) (Found: C, 40.7; H, 5.00; Cl, 26.1; N, 7.9. C₁₈H₁₃Cl₂N₂O₃Sn requires C, 39.8; H, 4.6; Cl, 26.1; N, 7.7%).

[Sn(mpap)(dmap)]⁵⁺ — To a dichloromethane (6 cm³) solution of complex 1 (100 mg, 0.23 mmol) was added an excess of dimethyl sulfoxide and stirred at room temperature for 4 h a new suspension was obtained. After filtration, complex 5 was obtained as a yellow solid. Yield 82%, m.p. 176 °C. ν(νOH) 3470 cm⁻¹. 6(¹H) 8.00-7.12 (m, 7 H, Ph), 2.56 (s, 3 H, Me) and 2.44 (s, 3 H, Me) (Found: C, 40.7; H, 5.00; Cl, 26.1; N, 7.9. C₁₈H₁₃Cl₂N₂O₃Sn requires C, 39.8; H, 4.6; Cl, 26.1; N, 7.7%).
Table 3 Atomic coordinates (x10^4) for compound 7

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[Sn(mpap)Cl2(O,CMe)2] 10.—To a suspension of complex 6 (100 mg, 0.11 mmol) in dichloromethane (20 cm³) was added (MeCO)2O (62 mg, 0.61 mmol); the suspension was stirred for 5 h and then filtered. The solution was evaporated under vacuum (1 cm³) and the residue was added to precipitate complex 11. Yield 56%. (Found: C, 41.3; H, 4.8; N, 5.6%. C21H23N202Sn requires C, 41.6; H, 4.8; N, 5.5%.

[Sn(mpap)Cl2] 8.—(a) To a solution of [Sn(mpap)ph2Cl] (80 mg, 0.15 mmol) in dichloromethane (7 cm³) was added 7 (47 mg, 0.15 mmol); the resulting suspension was stirred at room temperature for 4 h and filtered over Celite. The filtrate was concentrated to dryness and the residue was added to precipitate complex 11. Yield 81%. (Found: C, 62.9; H, 4.6; N, 5.8. C21H23N20Sn requires C, 62.6; H, 4.7; N, 5.8%.

X-Ray Structure Determination of Compound 6 (Diethyl Ether Solvate).—Crystal data. C21H23N202Sn·0.5C2H5OH·M = 1017.0, monoclinic, space group P21/c, a = 20.278(7), b = 11.073(4), c = 21.016(7) Å, β = 101.82(3), V = 4619(3) Å³, Z = 4, Dc = 1.46 Mg m⁻³, λ(Mo-Kα) = 0.7109 Å, µ = 1.36 mm⁻¹, F(000) = 2052, T = 295 °C.

Data collection and reduction. A yellow prism ca. 0.6 × 0.95 × 0.3 mm was mounted in inert oil on a glass fibre and transferred to the cold gas stream of the diffractometer (Siemens R3 with LT-2 low-temperature attachment). A total of 9372 reflections were measured to 2θmax 50°, of which 8119 were unique (Rint 0.025) and 6588 considered observed [F > 2σ(F)]. An absorption correction based on ψ scans was applied, with transmission factors 0.61-0.89. Cell constants were refined from 60 reflections of 50 reflections in the 2θ range 20-22°.

Structure solution and refinement. The structure was solved by direct methods (to locate the tin atoms) and subsequent tangent recycling. Two ordered molecules of diethyl ether, hydrogen bonded to the complex, were located, and another molecule was found to be disordered over a symmetry centre. Hydrogen atoms were included in the refinement using a riding model, except for the disordered solvent H (not included) and the hydroxyl H, which were refined subject to the O–H bond length restraint 0.85 ± 0.02 Å. Anisotropic refinement on F led to a final R value of 0.039, R' = 0.048. The weighting scheme was w⁻¹ = σ²(F) + 0.000 35 F². 466 Parameters; S 1.7; maximum Δρ 0.1; maximum Δρ 1.5 e Å⁻³. The crystallographic program system Siemens SHELXTL PLUS was used. Final atomic coordinates are given in Table 1, selected bond lengths and angles in Table 2.

X-Ray Structure Determination of Compound 7 (Diethyl Ether Solvate).—Compound 7 crystallizes in the orthorhombic space group C222, with a = 14.644(5), b = 23.840(7), c = 13.640(7) Å (at −95 °C, Z = 4). Data were collected as above. The structure was refined to R = 0.089. A region of unidentified electron density was tentatively identified as an ether molecule, but two large difference peaks were impossible close to ring carbon atoms. Attempts to refine the structure in a transformed cell of lower symmetry, P21, with a = c, were similarly unsuccessful (such structures can falsely simulate space group C222,1). It is probable that the crystal was twinned. In view of the difficulties the bond lengths and angles must be unreliable, and we do not present them. The atom coordinates are given in Table 3, without c.s.d.s, in Table 3.

Acknowledgements


References

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