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Synthesis, Characterization, and Reactivity of Bivalent Tin(II) with 4-Tert-butylphenol

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Abstract

Bivalent tin(II)-4-tert. butylphenoxide of composition $Sn(OC_6H_4X\text{-}4)_2$(I), where X = Bu^t, has been synthesized by the reaction of stannous chloride ($SnCl_2$) with bimolar amounts of 4-tert. butyl phenol ($HOC_6H_4Bu^t\text{-}4$) in the presence of the base, diethyl amine, in tetrahydrofuran (THF) solvent. The resulting complex was characterized by elemental analysis, molecular weight determination, molar conductance measurement, IR, and ^1H NMR spectral studies. The reactivity of the newly synthesized complex (I) with $HgCl_2$ has been investigated using potentiometric techniques, followed by an actual reaction between the complex ($Sn(OC_6H_4X\text{-}4)_2$) and mercuric chloride ($HgCl_2$), resulting in the formation of a new Sn(IV) complex of composition $SnCl_2(OC_6H_4Bu^t\text{-}4)_2$. The quantitative formation of a grayish compound identified as Hg_2Cl_2 as a byproduct was observed. Elemental analysis of the solid compound isolated from the above solution corresponded well with its stoichiometric formulation as $SnCl_2(OC_6H_4Bu^t\text{-}4)_2$ and was later confirmed by molecular weight determination, conductance measurement, IR, and ^1H NMR spectral studies. Conductometric titration between complex (I) and the sodium salt of 4-tert. butylphenol suggests the formation of a double phenoxide of composition $Na_2[Sn(OC_6H_4Bu^t\text{-}4)]_4$. Further investigations into the complex's stability and potential applications in catalytic processes are underway, promising new insights into the behavior of tin(II) compounds in various chemical environments. This study enhances the understanding of the reactivity and complexation behavior of tin(II) with organic ligands, contributing to the broader field of coordination chemistry and its practical applications.

Keywords: Tin(II) phenoxide, 4-tert- butyl phenol, reactivity, NMR, IR Spectra

INTRODUCTION

The chemistry of tin has developed into one of the most exciting area of active industrial and academic research in the main group chemistry and there has been a continuous interest in the preparation of tin(II) compounds, because of the diverse applications of tin oxide thin films [1–4]. A number of tin(II) [5]. A series of colored di-t-butylphenoxides of bivalent tin, germanium and lead are known to exist as discrete monomer in the crystalline state at ambient temperature [6]. Span and coworkers [7] have investigated the variation of organic functionality bivalent tin alkoxide and aryloxide complexes, have prompted us to attempt the synthesis of and dipolar properties of the over layer of tin phenoxide complexes covalently bound to indium tin oxide (ITO) surface and resulting surface modification. The interesting applications of bivalent tin(II)-4-tert butylphenoxide and its characterization . Compared to a number of reports on the stable covalent double alkoxides of different metals (8-10), very little attention has been focused on the isolation of double phenoxides of metals.

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Malhotra and coworkers [11], in one of their reports have described the nature of double phenoxides of niobium(V) and tantalum(V). It is therefore worthwhile to undertake the reactivity of bivalent tin aryloxides isolated in the present studies with alkali metal aryloxides.

Experimental: Experimental

Stannous chloride ($SnCl_2$), 4-tert-butylphenol ($HOC_6H_4Bu^t$-4), diethyl amine, tetrahydrofuran (THF), mercuric chloride ($HgCl_2$), was obtained from commercial suppliers and used as received without further purification.

Synthesis of $Sn(OC_6H_4Bu^t$-4)$_2$(I): In a dry, inert atmosphere, a solution of stannous chloride (0.5 mmol) in THF (20 mL) was prepared and added dropwise to a solution of 4-tert-butylphenol (1.0 mmol) in THF (20 mL) containing diethyl amine (0.5 mmol) as a base. The reaction mixture was stirred at room temperature for 4 hours. The resulting precipitate was filtered, washed with THF, and dried under vacuum to yield the bivalent tin(II) complex $Sn(OC_6H_4Bu^t$-4)$_2$(I).

Characterization:

Tin content in compound was determined as SnO_2. A Beckman thermometer was used to determine the molecular weight in nitrobenzene cryoscopically, and an Elico-conductivity bridge (CM Type 82-T) was used to measure conductance in the same solvent using 10^{-3}M solution. The Nicolet 5700 FTIR spectrometer was used to record the IR spectra of the KBr pellets. Using TMS as an internal standard, ^{1}H NMR spectra were obtained on a Bruker-AC 400 MHz spectrometer. Potentiometric titration of $Sn(OC_6H_4Bu^t$-4)$_2$ vs. $HgCl_2$ was carried out using Toshiniwal potentiometer

Reaction with $HgCl_2$: To study the reactivity of $Sn(OC_6H_4Bu^t$-4)$_2$(I) with mercuric chloride, a solution of the complex (0.5 mmol) in THF (20 mL) was added to a solution of $HgCl_2$ (0.5 mmol) in THF (20 mL). The reaction mixture was stirred at room temperature for 6 hours. The resulting solution was filtered, and the precipitate was washed with THF and dried. The formation of $SnCl_2(OC_6H_4Bu^t$-4)$_2$ was confirmed by elemental analysis, molecular weight determination, conductance measurements, IR, and ^{1}H NMR spectral studies.

Conductometric Titration: Conductometric titrations were conducted by adding a solution of the sodium salt of 4-tert-butylphenol (0.5 mmol) to a solution of $Sn(OC_6H_4Bu^t$-4)$_2$(I) (0.5 mmol) in acetonitrile. The titrations were monitored by measuring the conductance until a constant value was reached, indicating the formation of $Na_2[Sn(OC_6H_4Bu^t$-4)$]_4$.

Isolation and Analysis: The solid products obtained from the reactions were analyzed by elemental analysis, molecular weight determination, conductance measurements, IR spectroscopy, and ^{1}H NMR spectroscopy to confirm their compositions and stoichiometric formulations.

MATERIALS

The hydrated sample (30g) was heated with acetic anhydride to produce anhydrous stannous chloride (m.p 244^{o}C), as described in the literature [12]. Mercuric chloride (AR) was used as such without further purification while 4- tert butyl phenol was used after re-crystallization from ether (m.p94^{o}C). Sodium salt of 4-tertbutylphenol, $NaOC_6H_4Bu^t$-4 was obtained as a white solid by the reaction of sodium metal with 4-tertbutylphenol in equimolar amounts in benzene with vigorous stirring.

RESULTS AND DISCUSSION

Direct reaction of anhydrous stannous chloride dissolved in tetrahydrofuran with 4-tert. butyl phenol did not result in the evolution of expected hydrogen chloride gas even under reflux. Alternatively therefore, stannous chloride was then allowed to react with calculated amount of sodium salt of corresponding 4-substituted phenol in tetrahydrofuran followed by heating under reflux. Although, in this case separation of sodium chloride did take place as follows:

$$SnCl_2 + 2NaOC_6H_4X\text{-}4 \xrightarrow[\text{Reflux}]{\text{THF}} Sn(OC_6H_4X\text{-}4)_2 + 2NaCl\downarrow$$

Where X = Bu^t

Yet the yield of the desired compound isolated from the solution was very less compared to the expected one. Therefore this method also had to be abandoned. For the preparation of aryloxides of tin(II) therefore, the method involving the reaction of anhydrous stannous chloride with calculated amount of corresponding 4-substituted phenol in the presence of predetermined amount of a base, diethyl amine in 1:2:2 molar ratio, was used. All the three components dissolved separately in tetrahydrofuran were mixed together with continuous stirring. From the resulting mixture solution quantitative amount of a white solid, later identified as diethylaminehydrochloride ($Et_2NH.HCl$) from its melting point separated out during the course of reaction. The formation of the desired compounds has been rationalized in terms of the following reaction:

$$SnCl_2 + 2\,OHC_6H_4 - Bu^t - 4 + 2Et_2NH \xrightarrow{THF} Sn(OC_6H_4 - Bu^t - 4)_2 + 2Et_2NH.HCl\downarrow$$

The stoichiometric composition of the solid compound, isolated from the solution has been established by elemental analysis % found (calculated); Sn = 28.39(28.53); C = 56.85(57.55); H = 6.21(6.23). The compound is creamish yellow solid. It does not melt but decomposes at 55°C. It is only sparingly soluble in methanol and acetonitrile. The compound's millimolar solution in nitrobenzene has a very low molar conductance value (0.92 ohm-1cm2mol-1) and is therefore thought to act as a non-electrolyte in this solvent. Remarkably, the chemical does not re-dissolve in THF solvent, indicating that it may have polymerized in the solid state even after being isolated from the solvent.

I.R. Spectra

Information for the formation of $Sn(OC_6H_4Bu^t\text{-}4)_2$ has been obtained from its infra-red spectrum recorded in 4000-250 cm^{-1} region. The broad band observed in 3420-3390cm^{-1} region in pure 4-tert butylphenol due to phenolic υOH mode [13, 14] is missing while the bands in 1600-1400cm^{-1} region attributed to υ(C=C) in the phenolic ring have been found to shift slightly towards higher wave numbers possibly due to increased ring conjugation brought about by complex formation. The most important and diagnostic band due to υ_{ring} C-O mode reported to occur around 1225cm^{-1} in pure 4-tert. butylphenol appeared at 1179cm^{-1} in the complex. This substantial shift to a lower wave number has been explained in terms of the bonding between phenolic oxygen and tin, which is further supported by the emergence of completely new bands in the 620–490 cm^{-1} range that are attributed to υ(Sn–O) but are not present in the ligand. Modes [15, 16].

I.R. Spectral data of ligand and complex

Here is explanation.

$OHC_6H_4\,Bu^t\text{-}4$: 3420, 3390, 3060, 3020, 1628, 1595, 1515, 1428, 1365, 1325, 1225, 1180, 1120, 1092, 1025, 980, 940, 850, 825, 790, 720, 657, 600.

$Sn(OC_6H_4Bu^t\text{-}4)_2$: 3118, 3060, 2958, 2864, 2681, 2363, 1877, 1750, 1634, 1508, 1553, 1459, 1390, 1362, 1179, 1108, 1050, 1020, 923, 832, 680, 547.

^{1}HNMR Spectra

Further information for the formation of tin(II) aryloxide has been obtained from their room temperature ^{1}H NMR spectra. The changes observed in the proton resonances of the complexes compared to those of the free phenols have provided evidences for the formation of these complexes.

The free 4-tert. butyl phenol is known to display signals at δ4.91 and δ1.28ppm attributed to phenolic OH and t-butyl protons. The complex of composition $Sn(OC_6H_4Bu^t\text{-}4)_2$ did not show any signal at δ4.91ppm confirming thereby their deprotonation during the reaction and formation of the complex. The signal at δ1.28 due to t-butyl protons undergoes slight upfield shift and appeared at δ1.27ppm. Further, a perusal of signals due to phenyl ring protons shows two doublets of equal intensity due to H-C-C-H vicinal coupling for ortho and meta ring protons with peaks centered at δ6.75 and 7.23ppm in pure phenol have been found to shift to δ6.74 and 7.17ppm in $Sn(OC_6H_4Bu^t\text{-}4)_2$. The observed upfield shifts have tentatively been assigned to overall π-bonding properties of aryloxo ligands as also reported by Clark and coworkers (17) in tantalum(IV) aryloxide complexes.

Reactivity

In the present studies, reactivity of bivalent tin(II)-4-substituted phenoxide has been investigated by carrying out their reactions with following reagents

1. Reaction with mercuric chloride
2. Reaction with sodium salt of 4-substituted phenols ($NaOC_6H_4X\text{-}4$) where $X=Bu^t$

Reaction of $Sn(OC_6H_4Bu^t\text{-}4)_2$ with Mercuric chloride

The well known redox reaction of stannous chloride with mercuric chloride 18] has been the key factor for understanding the reactivity of $Sn(OC_6H_4Bu^t\text{-}4)_2$ with mercuric chloride.

$$SnCl_2 + 2HgCl_2 \underset{}{\overset{MeOH}{\rightleftharpoons}} SnCl_4 + Hg_2Cl_2$$

In order to explore the possibility of such a reaction, potentiometric titration between $Sn(OC_6H_4Bu^t\text{-}4)_2$ and $HgCl_2$ in methanol was carried out. Potential – composition curve shows a sharp break at 1:2 molar ratio as shown in Figure 1.

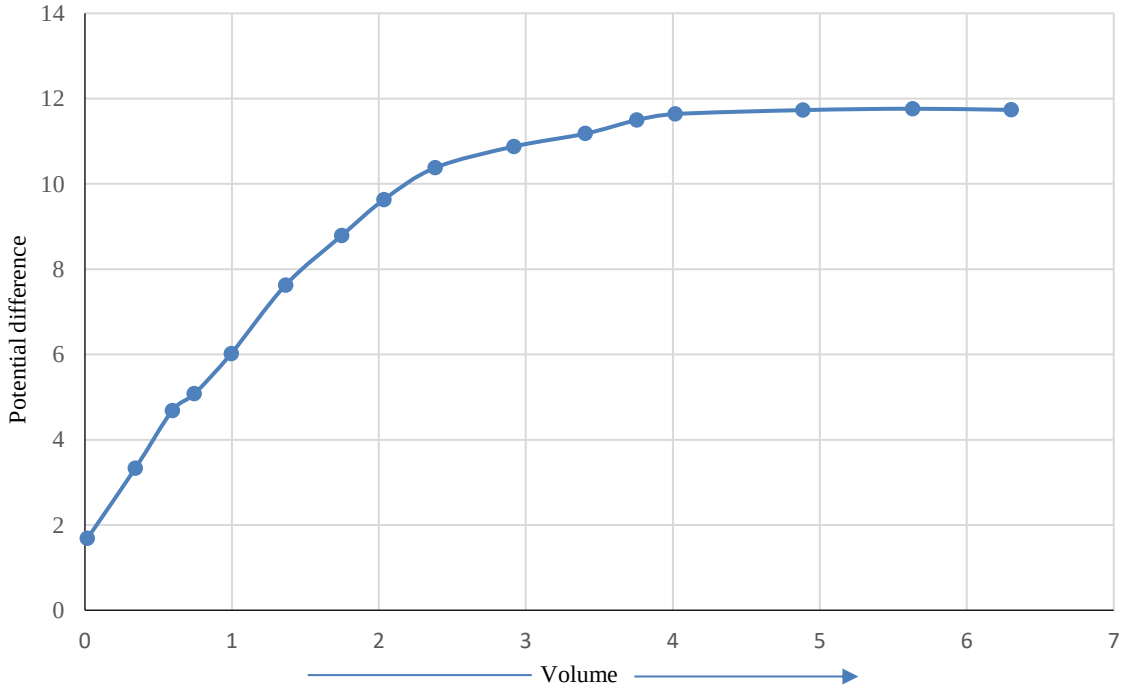

Figure 1. Potentiometric Titration of $Sn(OC_6H_4Bu^t\text{-}4)_2$ vs $HgCl_2$.

Based on this preliminary potentiometric study, reaction between $Sn(OC_6H_4Bu^t\text{-}4)_2$ and mercuric chloride in methanol led to the formation of $SnCl_2(OC_6H_4Bu^t\text{-}4)_2$ as :

$$Sn(OC_6H_4X\text{-}4)_2 + 2HgCl_2 \xrightarrow{MeOH} SnCl_2(OC_6H_4X\text{-}4)_2 + Hg_2Cl_2\downarrow$$

Where X= But

The quantitative formation of a grayish compound identified as Hg_2Cl_2 as byproduct was observed. Elemental analysis of the solid compound isolated from the above solution (% found (calculated) Sn=24.12% (24.43%); Cl=14.20% (14.37%) corresponded well with its stoichiometric formulation as $SnCl_2(OC_6H_4Bu^t\text{-}4)_2$. this complex was latter characterized by spectroscopic techniques Figure 1

Double phenoxide formation

Having synthesized and characterized $Sn(OC_6H_4Bu^t\text{-}4)_2$, it was quite interesting to explore the possibility of formation of double phenoxide by reacting it with alkali metal phenoxide. For this purpose, conductometric titration of $Sn(OC_6H_4Bu^t\text{-}4)_2$ vs. $NaOC_6H_4Bu^t\text{-}4$ in nitrobenzene was carried out at 25±1°C. The conductance- composition curve shows break at 1:2 molar ratio of $Sn(OC_6H_4Bu^t\text{-}4)_2$:$NaOC_6H_4Bu^t$ which suggest the formation of compound of 1:2 stoichiometry.

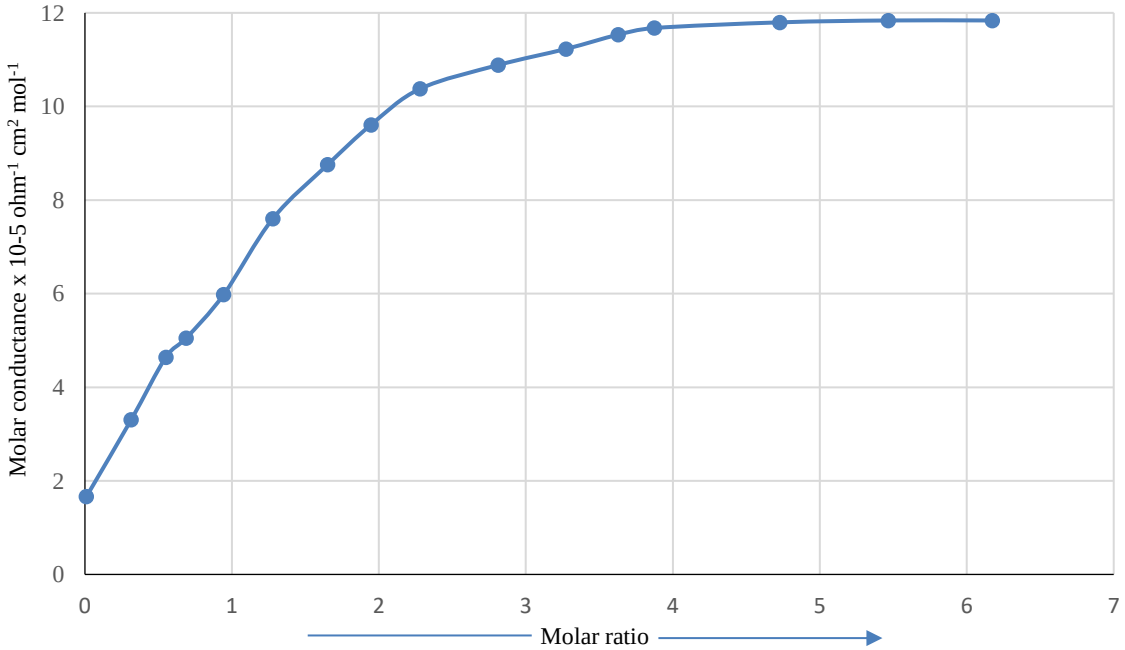

Figure 2. Conductometric Titration of $Sn(OC_6H_4Bu^t\text{-}4)_2$ vs $NaOC_6H_4Bu^t\text{-}4$

Inferred from this, compound of composition $Na_2[Sn(OC_6H_4Bu^t\text{-}4)_4]$ was prepared by reacting a known amount of tin (II)-4-tert. butylphenoxide with bimolar amount of sodium salt of 4-tert. butylphenol in accordance with the equation:

$$Sn(OC_6H_4X\text{-}4)_2 + 2\,NaOC_6H_4X\text{-}4 \xrightarrow{PhNO_2} Na_2Sn(OC_6H_4X\text{-}4)_4$$

$$Na_2Sn(OC_6H_4X\text{-}4)_4 \rightleftharpoons 2Na^+ + [Sn(OC_6H_4X\text{-}4)_4]^{2-}$$

(Where X=Bu^t)

The complex is brown colored solid. The millimolar solution of this compound in nitrobenzene has a molar conductance value of 10-12$\Omega^{-1}cm^2mol^{-1}$, indicating that it is a reasonably excellent electrolyte Figure 2.

CONCLUSION

In conclusion, a new tin(II) complex was successfully synthesized and thoroughly characterized using a variety of spectroscopic methods, including NMR and IR spectroscopy, which provided detailed information on its structural and electronic properties. The reactivity of this newly synthesized complex was extensively studied by reacting it with mercuric chloride and the sodium salt of 4-tert-butylphenol. This resulted in the formation of a tin(IV) complex and a double phenoxide salt, revealing important insights into the behavior of tin(II) compounds in oxidation and complexation processes. The formation of these new species highlights the versatile reactivity of tin(II) complexes and their potential applications in various chemical transformations. These findings contribute to a deeper understanding of tin-based coordination chemistry and open avenues for further research into the applications of tin complexes in catalysis and material science. Future work will focus on exploring the catalytic properties and stability of these complexes in different reaction environments, as well as their potential use in industrial applications.

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