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Four coordinate tin complexes: Synthesis, characterization, thermodynamic and theoretical calculations



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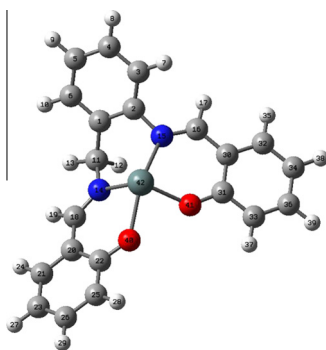
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HIGHLIGHTS

- Synthesis and characterization of two new four coordinate Sn(IV) complexes.
- Thermodynamic studies of twelve systems involving the synthesized Sn(IV) complexes.
- *Ab initio* calculation to verify the proper structure.

GRAPHICAL ABSTRACT

Two Sn(IV) complexes were synthesized and characterized by UV-Vis, FT-IR, ^1H NMR, ^{13}C NMR, ^{119}Sn NMR spectroscopies, mass spectrometry and elemental analysis. The thermodynamic formation constants and DFT calculations were carried out to interpret the structure of the complexes.



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ABSTRACT

In this work, two new Sn(IV) complexes, $[\text{SnL}^{\text{A}}]\text{Cl}_2$ where $(\text{L}^{\text{A}})^{2-}$ is the deprotonated form of 5-A-salabza- $\text{H}_2 = \text{N,N}'$ -bis(salicylidene)-2-aminobenzylamine and $\text{A} = 5\text{-OMe}, 5\text{-H}, 5\text{-NO}_2, 5\text{-Br}$, were synthesized and fully characterized by UV-Vis, FT-IR, ^1H NMR, ^{13}C NMR, ^{119}Sn NMR spectroscopies, mass spectrometry and elemental analysis. The thermodynamic formation constants of the complexes were determined spectrophotometrically at 25 °C in acetonitrile. The trend of formation constants of the complexes are as: $5\text{-OMe} > 5\text{-H} > 5\text{-NO}_2 > 5\text{-Br}$ and $\text{Ph}_2\text{SnCl}_2 > \text{Me}_2\text{SnCl}_2 > \text{n-Bu}_2\text{SnCl}_2$. DFT/B3LYP molecular orbital calculations were carried out for the 5-H substituent isomer, $[\text{SnL}^{\text{A}}]^{2+}$, in an attempt to explain the structure of complexes. The optimized resulting geometries, vibrational frequencies and the NMR resonances of the complexes are discussed.

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Introduction

The study of coordination chemistry of tin has received much attention due to its various geometries and coordination numbers known for both inorganic and organometallic complexes [1,2].

Especially, tin(IV) is known to form stable complexes with oxygen, sulfur, carbon and nitrogen containing ligands [3].

The number and diversity of nitrogen and oxygen chelating agents used to prepare new coordination and organometallic compounds have increased rapidly during the past few years [4–10]. Various Schiff bases and their substituted derivatives have been investigated frequently. These compounds have received much attention because (1) they provide an interesting series of ligands whose properties can be greatly modified by introducing different

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substituents, thereby causing a variation in the ultimate donor properties, (II) the interaction of these donors with metal ions give complexes of different geometries and properties, and (III) these complexes are potentially biologically active. Keeping this in view, it was considered worthwhile to synthesize tin complexes of some stereochemical as well as biological importance.

Tin(IV) complexes have been the subject of interest for some times because of their commercial and biomedical applications [11]. It has been observed that several organotin complexes are effective anti-microbial [12], antifouling [13] and antiviral agents. They are also used commercially as fungicides, bactericides, acaricides; agriculture and industrial biocides [14].

As an extension of the studies of Schiff base-tin(IV) complexes, the synthesis and characterization of two new complexes and the thermodynamic studies of twelve systems (four Schiff bases with three tin compounds) have been investigated here. In addition to the importance of the experimental studies, it is crucial to investigate the theoretical behavior of target complex to find the structural characteristic. The structure of the complex can be studied by the *ab initio* methods to find the electronically stable structure.

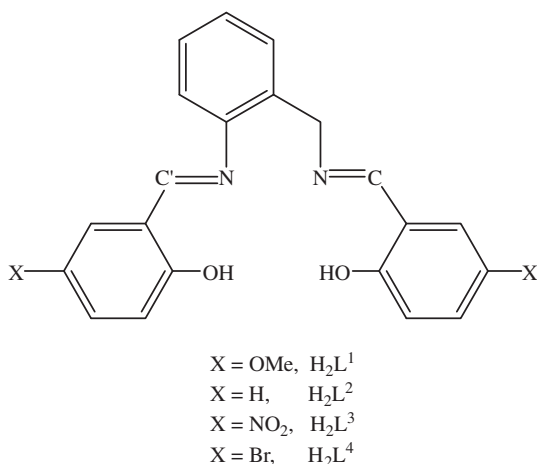
Experimental

Materials and physical measurements

All reagents and solvents were commercial products and were purchased from Aldrich, Alfa Aesar or Acros and used as received. The elemental analyses were carried out on a Thermo Finnigan-Flash-1200. The electronic spectra were recorded on Rayleigh UV-1600 spectrophotometer. FT-IR spectra were recorded on KBr using a Rayleigh WQF-510 infrared spectrophotometer. The mass spectra were obtained on a Agilent Technologies 5975C, inert MS-D instrument. ^1H NMR spectra were recorded on a Bruker Avance 200 (DPX) while ^{13}C and ^{119}Sn NMR spectra were recorded on a Bruker Avance 300 spectrometer. The ^1H and ^{13}C NMR chemical shifts in ppm are reported from tetramethylsilan (TMS) and ^{119}Sn NMR spectra were measured relative to SnCl_2 .

Synthesis of the ligands

The Schiff bases were prepared according to the literature method [15]. Melting points, elemental compositions and the spectral characterizations such as IR, ^1H NMR, UV-Vis spectroscopy and mass spectrometry of the prepared Schiff bases are in good



Scheme 1. The structure of ligands.

agreement with previous reports [15]. The prepared Schiff bases have the structural formula shown in Scheme 1.

Synthesis of the Sn(IV) complexes

To a hot methanolic solution of KOH (2 mmol), 1 mmol of ligand in dichloromethane was added with constant stirring and refluxed for 40 min. Then, excess amount of Ph_2SnCl_2 in dichloromethane was added dropwise and refluxed overnight. After removing the solvent, the product was separated and washed with dichloromethane, methanol and water. Four ligands were examined with Me_2SnCl_2 , $n\text{-Bu}_2\text{SnCl}_2$ and Ph_2SnCl_2 , but just $[\text{SnL}^1]\text{Cl}_2$ and $[\text{SnL}^2]\text{Cl}_2$ (Scheme 1) were separated and all attempts for preparing of other complexes were unsuccessful.

$[\text{SnL}^1]\text{Cl}_2 \cdot 0.5\text{H}_2\text{O} \cdot 2\text{CH}_2\text{Cl}_2$

Orange crystal (72%); m.p. 277 °C, Elemental Anal. Calc. for $\text{C}_{25}\text{H}_{25}\text{N}_2\text{O}_5\text{Cl}_4\text{Sn}$: C, 39.67; H, 3.33; N, 3.70; Found: C, 39.70; H, 2.98; N, 4.05. Molar conductivity ($1 \times 10^{-3} \text{ mol L}^{-1}$, DMSO): $137 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. ^1H NMR (DMSO- d_6): $\delta = 8.94$ (s, 1H, N=CH); 8.87 (s, 1H, N=CH'); 7.64–6.88 (m, 10H, H-Ar); 5.26 (s, 2H, CH_2); 3.81 (s, 3H, OCH_3); 3.73 (s, 3H, OCH_3') ppm. ^{13}C NMR (DMSO- d_6): $\delta = 172.34$ (N=C); 171.77 (N=C'); 160.54 (C–O); 160.01 (C–O'); 151.52, 151.12, 144.90, 130.63, 129.88, 128.94, 127.73, 126.73, 125.38, 124.57, 123.23, 119.10, 118.65, 118.29, 117.12, 116.83 ($\text{C}_{\text{aromatic}}$); 59.59 (CH_2); 55.63 (OCH_3); 55.54 (OCH_3') ppm. ^{119}Sn NMR (DMSO- d_6): $\delta = -102.70$ ppm. FT-IR (KBr): 3423 ($\nu_{\text{O-H}}$); 3064 ($\nu_{\text{C-H}}$, aromatic); 2995, 2931 ($\nu_{\text{C-H}}$, aliphatic); 1631, 1603 ($\nu_{\text{C=N}}$); 1589–1479 ($\nu_{\text{C=C}}$); 1277 ($\nu_{\text{C-O}}$); 750 ($\nu_{\text{Sn-N}}$); 492 ($\nu_{\text{Sn-O}}$) cm^{-1} . UV-Vis (λ_{max} , nm, CH_3CN , ϵ , $\text{M}^{-1} \text{ cm}^{-1}$): 249 (27330); 283 (17234); 315 (10050), 405 (6578). MS (m/z): 57, 83, 111, 137, 171, 194, 211, 236, 264, 285, 313, 339, 368, 395, 444, 507.

$[\text{SnL}^2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$

Yellow-green crystal (77%), m.p. 306 °C, Elemental Anal. Calc. for $\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_4\text{Cl}_2\text{Sn}$: C, 45.53; H, 3.64; N, 5.06; Found: C, 45.27; H, 3.35; N, 4.82. Molar conductivity ($1 \times 10^{-3} \text{ mol L}^{-1}$, DMSO): $137 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. ^1H NMR (DMSO- d_6): $\delta = 8.99$ (s, 1H, N=CH); 8.89 (s, 1H, N=CH'); 7.98–6.81 (m, 12H, H-Ar); 5.28 (s, 2H, CH_2) ppm. ^{13}C NMR (DMSO- d_6): $\delta = 172.80$ (N=C); 172.15 (N=C'); 165.84 (C–O); 165.44 (C–O'); 144.77, 138.15, 137.03, 136.07, 134.70, 130.64, 129.95, 128.23, 127.78, 127.26, 124.66, 122.23, 119.78, 119.24, 118.73, 117.57 ($\text{C}_{\text{aromatic}}$); 59.50 (CH_2) ppm. ^{119}Sn NMR (DMSO- d_6): $\delta = -102.54$ ppm. FT-IR (KBr): 3419 ($\nu_{\text{O-H}}$); 3049 ($\nu_{\text{C-H}}$, aromatic); 2927 ($\nu_{\text{C-H}}$, aliphatic); 1626, 1606 ($\nu_{\text{C=N}}$); 1579–1431 ($\nu_{\text{C=C}}$); 1280 ($\nu_{\text{C-O}}$); 696 ($\nu_{\text{Sn-N}}$); 449 ($\nu_{\text{Sn-O}}$) cm^{-1} . UV-Vis (λ_{max} , nm, CH_3CN , ϵ , $\text{M}^{-1} \text{ cm}^{-1}$): 277 (11644); 310 (7018); 365 (4692). MS (m/z): 51, 77, 97, 119, 154, 196, 231, 308, 344, 368, 447.

Thermodynamic studies of complex formation

Formation constant measurements were determined by UV-Vis absorption spectroscopy through titration of the ligands with various concentrations of organotin(IV) chloride at 25 (± 0.1) °C. In a typical experiment, 3 ml of the ligand solution ($5 \times 10^{-5} \text{ M}$) was transferred into thermodynamic cell compartment of UV-Vis instrument and titrated by the tin(IV) solution. The titration was performed with addition of aliquot amounts of the titrant with Hamilton μL syringe to the ligand solution. The absorption measurements were carried out at various wavelengths where the difference in absorptions was the maximum after equilibrium. The final spectra of products showed different absorption bands from the free ligands, while the Sn(IV) solutions showed no absorption at any wavelength. As an example, the variation of the electronic spectra for H_2L^2 , titrated with various concentrations of Bu_2SnCl_2

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