

새로운 유기주석 착물의 합성과 특성: 경쟁적인 N, O 및 S 주개 리간드에 기초한 Di(*n*-butyl)chloro[5-(*p*-dimethylaminobenzylidene)rhodanine]tin(IV)

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Synthesis and Characterization of a Novel Organotin Complex: Di(*n*-butyl)chloro[5-(*p*-dimethylaminobenzylidene)rhodanine]tin(IV) Based on a Competing N, O, and S Donor Ligand

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요약. 새로운 유기주석(IV) 착물을 Bu_2SnCl_2 과 N, O 및 S 주개 리간드인 5-(*p*-dimethylaminobenzylidene)rhodanine(HL)로부터 제조하였다. 염기 존재 하에 리간드는 탈양성자화되며, SnBuCl_2L 의 분자식을 갖는 착물이 형성되었다. 이 착물은 IR, ^1H NMR, ^{119}Sn NMR 및 원소분석을 통하여 전반적으로 특성을 분석하였다. 분광학적인 데이터로부터 리간드는 산소원자를 통하여 주석에 배위됨을 알았으며, 배위수가 4임을 용액에서 ^{119}Sn NMR 데이터에 의해 결정하였다.

주제어: Rhodanine 치환체, 유기주석착물, ^{119}Sn NMR, 주개 리간드

ABSTRACT. A novel organotin(IV) complex has been prepared from Bu_2SnCl_2 and the N, O and S donor ligand, 5-(*p*-dimethylaminobenzylidene)rhodanine (HL). The ligand is deprotonated in the presence of a base and the complex with the general formula SnBuCl_2L is formed. This complex was fully characterized by IR, ^1H NMR and ^{119}Sn NMR and elemental analysis. Spectroscopic data indicate the ligand is coordinated through the oxygen atom to the tin and the coordination number of four is supported by ^{119}Sn NMR data in solution.

Keywords: Rhodanine derivatives, Organotin complexes, ^{119}Sn NMR, Donor ligand

INTRODUCTION

Industrial, biological and agricultural applications of organotin compounds have shown an increasing growth during the last few years. They have been found to be biologically active as they show antitumour, antifouling, antimicrobial and antifungal activities.¹⁻⁹ The use of organotin compounds in industry has also risen as a result of their technical applications and their relatively low toxicological properties.¹⁰⁻¹²

The organotin(IV) halides have a marked tendency to increase their coordination number and are convenient systems for investigation of Lewis acid-base interactions. They have demonstrated a wide variety of coordination geometries around the Sn atom with a number of O-, N-, and S- donors and have a variety of biological effects depending on the number, type and arrangement of ligands

around the tin center.¹²⁻¹⁸

Despite of the extensive synthetic and structural reports on organotin(IV) complexes, those containing a ligand with suitable competing N, S and O reactive sites are still rare and have received much less attention.¹⁹⁻²³

Herein, we report the synthesis and characterization of a new complex of Bu_2SnCl_2 with 5-(*p*-dimethylaminobenzylidene)rhodanine (HL) (Fig. 1).

This compound has suitable competing donor centers (nitrogen, sulfur and oxygen) and seems to be a very good candidate for the formation of corresponding orga-

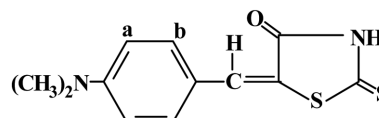


Fig. 1. Structure of HL.

notin complex and the evaluation of the nature of bonding with tin.

EXPERIMENTAL

Material and methods

The ligand (HL), Bu_2SnCl_2 and the solvents were obtained from the Merck chemical company. IR spectra were recorded on a Shimadzu 470 spectrometer in the 4000–400 cm^{-1} region with the samples as KBr discs. The ^1H and ^{119}Sn NMR spectra were recorded with a Bruker Avance DPZ500 spectrometer at 500.130 MHz and 186.496 MHz using TMS and SnMe_4 , as references, respectively. The C, H and N analysis were performed by the microanalytical service of the N.I.O.C. Research Institute of Petroleum Industry.

Synthesis of the complex

To a solution of the ligand (1 mmol, 0.264 g) in 20 ml CH_2Cl_2 a solution of NaOH (1 mmol, 0.040 g) in 10 ml of water was added at room temperature. This mixture was shaken for 10 min in a separating funnel. When the colour of the aqueous layer changes to dark red, two phases were separated. To the aqueous phase, a solution of Bu_2SnCl_2 (1 mmol, 0.303 g) in CH_2Cl_2 was added and the mixture was shaken in a separating funnel for 10 min. When the colour of organic layer was changed to the yellow colour, the organic layer was isolated and then the solvent was evaporated. The yellow product was washed with cold CHCl_3 and dried. Yield 73%, m.p. 170 °C. *Anal.* Calcd. for $\text{C}_{16}\text{H}_{20}\text{Cl}_2\text{N}_2\text{OS}_2\text{Sn}$: C, 37.7; H, 3.9; N, 5.5%. Found: C, 37.4; H, 3.6; N, 6.0%.

RESULTS AND DISCUSSIONS

5-(*p*-dimethylaminobenzylidene)rodanine, is deprotonated in the presence of a base, such as NaOH. The resulted anion can be shown in three resonance forms (Fig. 2).

The BuSnCl_2L complex was formed from the reaction of Bu_2SnCl_2 with an equimolar amount of this anionic ligand. The composition of the new complex has been confirmed by its analytical data. On the basis of this data,

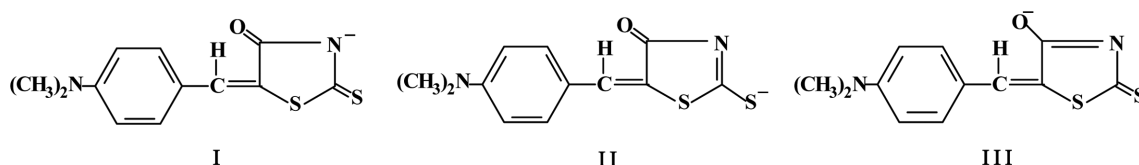


Fig. 2. Resonance forms for L^- .

Table 1. Selected IR data for the ligand and the complex (cm^{-1})

	$\nu\text{N-H}$	$\nu\text{C=O}$	$\nu\text{C=C}$	$\nu\text{C=N}$	$\nu\text{C=S}$	$\nu\text{Sn-O}$
HL	3460	1682	1565	-	1372	-
SnBuCl_2L	-	1628	1575	1610	1370	537

one butyl group was removed and the monoanionic ligand was substituted. This is an interesting result, because there is few reports about substitution of organic groups in organotin complexes.^{24,25} The nature of bonding in the complex was evaluated by the spectral data.

The IR spectra

Selected IR data for the free ligand and the complex are reported in Table 1. The band in 3460 cm^{-1} for N-H stretching vibrations in free ligand disappears in the infrared spectrum of the complex, in accordance with the deprotonation of the ligand. The stretching band $\nu(\text{C=S})$ band occurring at 1372 cm^{-1} in the ligand remains practically unchanged in the complex. This means that the ligand is not bound to the tin through the sulfur atom. Intense bands appeared at 2800–2900 cm^{-1} in IR spectrum of the complex are assigned to butyl group.

The strong $\nu(\text{C=O})$ band appearing in the 1682 cm^{-1} in free ligand is shifted considerably toward the lower energy in the complex and appeared at 1628 cm^{-1} . This indicates that the coordination of ligand to the tin center is taken place through the oxygen. Appearance of a new band at 1610 cm^{-1} is appeared in IR spectrum of the complex assigning to $\nu(\text{C=N})$ also supports the bonding of oxygen to the tin atom and involvement of the resonance form III. The band in 537 cm^{-1} can be assigned to $\nu(\text{Sn-O})$.²⁵⁻²⁸

A band assignable to $\nu(\text{C=C})$ stretching vibration at 1565 cm^{-1} in ligand is shifted to 1575 cm^{-1} upon coordination, indicating the resonance effect between C=O and C=C was decreased in the coordinated ligand and the double bond characterization of the C=C was increased.

The ^1H NMR spectra

Fig. 3a shows the ^1H NMR spectrum of complex. The ^1H NMR data for the ligand and its corresponding organotin(IV) complex has been reported in the Table 2. The

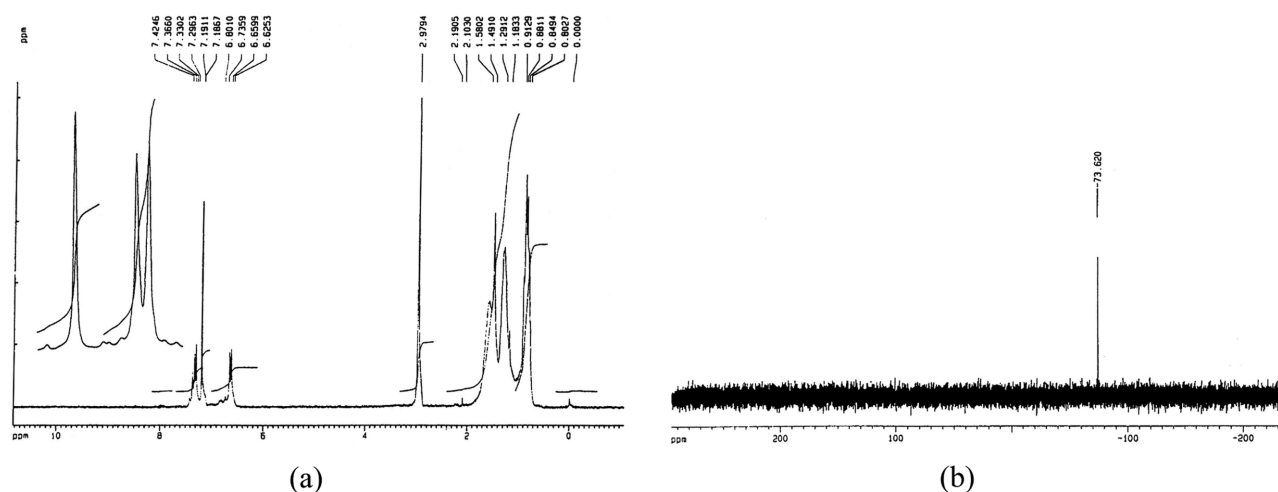


Fig. 3. (a) ^1H NMR (b) $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectra of the complex.

Table 2. ^1H NMR data for free ligand and complex in CDCl_3 (ppm)

	NH	C-H	H_a	H_b	$\text{N}(\text{CH}_3)_2$	Bu
HL	13.5(s)	7.52(s)	7.38(d)	6.78(d)	3.00(s)	-
SnBuCl_2L	-	7.42(s)	7.34(d)	6.63(d)	2.98(s)	1-1.3(m)

absence of the NH proton signal in the complex supports the removing of this hydrogen atom. Butyl protons attached with tin atom are observed in the range δ 1.0-1.3 ppm, as a complex multiplet. The $^2\text{J}(^{119}\text{Sn}-^1\text{H})$ value can not be extracted from the spectrum because of the complexity of the methylene multiplets.

The ^1H NMR spectrum of the complex also shows characteristic signals due to phenyl protons (H_a , H_b) and =C-H. In the ^1H NMR spectrum of ligand the N-methyl signal appears at 3.00 ppm as a singlet. It was observed that the chemical shift due to this group remains unchanged in the complex. This means that the ligand is not bound with tin through this nitrogen atom. If this bond was formed there would have been large shift for the N-methyl protons to the down field.

^{119}Sn NMR

$^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of the complex in CDCl_3 (Fig. 3b) shows only one sharp singlet in -73 ppm indicating the formation of a single species. This ^{119}Sn resonance appears at significantly lower frequency than that of Bu_2SnCl_2 (+122 ppm)²⁹ which implies a higher effective electron density at tin upon coordination to the ligand. The ^{119}Sn chemical shifts is influenced by the variation in the coordination number and bond angles at tin, by any $\text{d}\pi\text{-p}\pi$ bonding effect and by the presence of electronegative substituent.^{30,31} $\delta(^{119}\text{Sn})$ value for the complex is also in very

good agreement with those reported values for four-coordinated tin compounds.³²⁻³⁶

CONCLUSION

5-(*p*-dimethylaminobenzylidene)rodanine (HL) is coordinated to the tin in the deprotonated form III and only through the oxygen atom. One butyl group was removed and the complex was formed with 1:1 ratio of the tin compound and the ligand. The four coordinated tin in solution has also been supported by ^{119}Sn NMR data at room temperature.

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