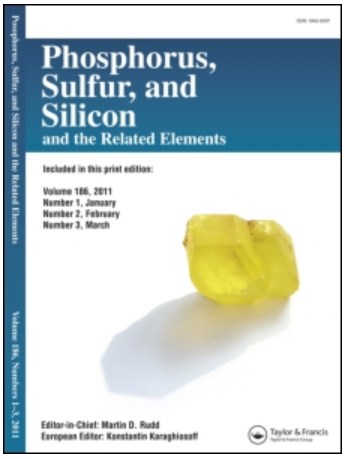

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Synthesis and Spectroscopic Investigations of New Schiff Base Complexes of Tin(IV)

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*The organotin(IV) chlorides SnR_2Cl_2 (R = Bu and Me) react with a new Schiff base (Hcdpen), obtained from the condensation of methyl-2-{N-(2′-aminoethane)}-amino-1-cyclopentenedithiocarboxylate and pyridine 2-carbaldehyde. The novel adducts $[SnMe_2Cl_2(Hcdpen)]$ (**1**) and $[SnBu_2Cl_2(Hcdpen)]$ (**2**) were characterized by elemental analysis, as well as by IR, ^1H NMR, and ^{119}Sn NMR spectroscopy. Spectroscopic studies show that, in the two new complexes Hcdpen acts as a monodentate neutral ligand and coordinates to the metal only via the pyridine nitrogen atom, while the imine nitrogen atom is not involved in the coordination to the tin. The ^{119}Sn NMR data are consistent with the presence of five-coordinated tin(IV) in solution.*

Keywords ^{119}Sn NMR; organotin(IV); pyridyl ligands; Schiff base; tin(IV)

INTRODUCTION

Schiff bases play an important role as ligands in metal coordination chemistry even after almost a century since their discovery. Modern chemists still prepare Schiff bases, and nowadays active and well-designed Schiff base ligands are considered as "privileged ligands." Schiff bases and their metal complexes have a variety of biological, clinical, analytical, and industrial applications and in addition play an important role in catalysis and organic synthesis.[1] There has been considerable interest in the design, synthesis, and application of unsymmetrical Schiff base ligands. This interest has been stimulated partly by the fact, that in many metalloproteins the metals are contained in a non-symmetrical environment, and by the modified properties of complexes derived from these ligands.[2–4]

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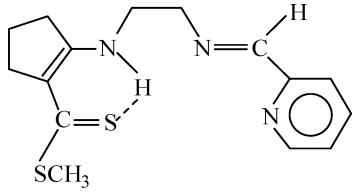
Attention has been devoted to Schiff base complexes of organotin(IV) moieties in view of their potential applications in medicinal chemistry and biotechnology and their structural variety.[5–7] Both aliphatic and aromatic Schiff bases in their neutral and deprotonated forms have been used to react with organotin(IV) halides; the complexes, that are formed, exhibit variable stoichiometry in the metal to ligand ratio and different modes of coordination.[8–10]

We report here the synthesis and characterization of novel complexes of diorganotin(IV) dichlorides with a new unsymmetrical Schiff base ligand containing a pyridine ring. Schiff bases incorporating a pyridine ring have received considerable attention in the literature because of their very important role in biological systems. They may also be used as analytical reagents for metals and as anti-inflammatory agents.[11] On the other hand, diorganotin(IV) dihalides and their complexes are becoming increasingly important in the area of antitumour activity and cancer chemotherapy. An important class of compounds in this area is diorganotin(IV) dichloride complexes with ligands containing nitrogen atoms as members of an aromatic ring, which act as donor atoms.[12] As a continuation of our studies on the interaction of organotin(IV) species with *S*-donor and *N*-donor ligands,[13] we have synthesized a Schiff base containing a pyridine moiety and have investigated its interaction with diorganotin(IV) compounds. The results of this study are reported here.

RESULTS AND DISCUSSION

The Schiff base used in this work, methyl-2-{*N*-[2-(2′-pyridyl)methyl-idynenitrilo] ethyl}amino-1-cyclopentenedithiocarboxylate (Hcdpen), is a conformationally flexible ligand, which is synthesized from the reaction of methyl-2-{*N*-(2′-aminoethane)}-amino-1-cyclopentene-dithiocarboxylate with pyridine 2-carbaldehyde. The new complexes were prepared by reaction of $SnMe_2Cl_2$ and $SnBu_2Cl_2$ with Hcdpen in MeOH. In these reactions only 1:1 adducts were obtained, even when an excess of the ligand was used. The composition of the new compounds was confirmed by their analytical data and the nature of bonding in the complexes was recognized by spectroscopic investigations.



Hcdpen

IR Spectra

In the IR spectrum of Hcdpen, the strong well resolved sharp bands at 1595, 1479, 1434, 1045, 615 cm^{-1} are assigned to the pyridine ring.[14] These signals show minor to significant shifts when compared with those of the complexes indicating the participation of the pyridine nitrogen atom in coordination to the tin. In particular the characteristic in plane deformation band of the pyridine ring found at 615 cm^{-1} in the free ligand shifts to the higher wavenumber ($\sim$22 cm^{-1}) in the complexes to indicate coordination of the ring nitrogen atom.[15] The azomethine C═N band, which appears at 1643 cm^{-1} in the IR spectrum of the ligand, is found at the same position in the spectra of the adducts. This observation indicates that the imine nitrogen atom is not involved in coordination to the tin atom. In the IR spectra of the adducts a new band at 420 cm^{-1} may be assigned to ν(Sn-N).[16]

NMR Spectra

Considering the orientation of the C═N groups with respect to the $-CH_2$-CH_2-bridge, Hcdpen can adopt *Z* or *E* conformation. The ^1H NMR spectrum of the ligand in $CDCl_3$ solution shows only one set of resonances for the pyridyl, imine, and methylene protons, indicating the presence of only one isomer. In the ^1H NMR spectrum of Hcdpen, the NH proton appears as a singlet at low field due to intramolecular hydrogen bonding. The presence of this signal at the same position in the NMR spectra of the complexes indicates that Hcdpen acts as a neutral ligand and that the amino group is not involved in coordination to the tin atom. In the ^1H NMR spectra of the complexes, the signals of the pyridine protons are shifted to low field; this applies in particular to the signal of the proton next to the nitrogen donor atom. This shift is due to a charge transfer from the pyridine nitrogen atom to the tin(IV) acceptor and confirms the coordination of the ligand *via* the pyridine ring. The lack of a downfield shift of the signal attributable to S-CH_3 indicates no participation of the —C═S group in coordination to the tin atom.[17] The signal attributable to the imine proton (HC═N) in the spectra of both complexes is not accompanied by $^{117/119}$Sn satellites; this is an indication that the corresponding nitrogen atom is not coordinated to tin(IV).[7] The ^1H NMR spectrum of **1** shows a singlet at 1.11 ppm accompanied by satellites with $^2J(^{119}Sn\text{-}^1H)$ larger than in uncomplexed $SnMe_2Cl_2$ ($^2J(^{117/119}Sn\text{-}^1H) = 65.7/68.7$ Hz[18]). Generally on complexation the magnitude of $^2J(^{119}Sn\text{-}^1H)$ increases and varies depending on the stereochemistry at the tin atom and on the nature of the ligand. The larger coupling constant indicates the higher coordination number

of tin. $^2J(^{119}Sn\text{-}^1H)$ for this compound (96.9 Hz) is typical of pentacoordinated methyltin(IV) compounds.[19] Substitution of the coupling constant in the Lockhart-Manders equation[20] gives a value 156.5° for the Me-Sn-Me angle. The $^2J(^{119}Sn\text{-}^1H)$ value for **2** cannot be extracted from the spectrum because of the complexity of the methylene multiplets.

The $^{119}Sn\{^1H\}$NMR spectra of the two complexes show one sharp singlet at −89.5 and −110.8 ppm for **1** and **2**, respectively. These resonances appear significantly at lower frequency than that of $SnMe_2Cl_2$ (+137 ppm) and $SnBu_2Cl_2$ (+123 ppm).[21,22] The ^{119}Sn chemical shifts are influenced by the variation in the coordination number and bond angles at the tin atom, by any $d\pi$-$p\pi$ bonding effect, and by the presence of electronegative substituents.[23] When the tin coordination number increases the ^{119}Sn signal moves to higher field. Based on the chemical shift ranges proposed empirically for organotin(IV) derivatives,[19,24,25] it appears reasonable to assume that in the two complexes the coordination number of the tin atom is five in solution. However, the values of these resonances are at the low field limit of this range. Perhaps the presence of a nitrogen atom in the coordination sphere of the tin shifts the signal towards more deshielded values.[26]

From spectroscopic studies, it is concluded that in the two new complexes Hcdpen acts as a monodentate ligand binding only through the nitrogen atom of the pyridine ring (Figure 1b) and this Sn-N interaction persists in $CDCl_3$ solution. Geometry optimization at MP3 level of theory using the HYPERCHEM package suggests a *Z* configuration for the ligand (Figure 1a). According to this configuration and owing to the restricted rotation about the C=N bond, a bidentate chelating coordination *via* both pyridine and imine nitrogen atoms is ruled out. This is consistent with the experimental results.

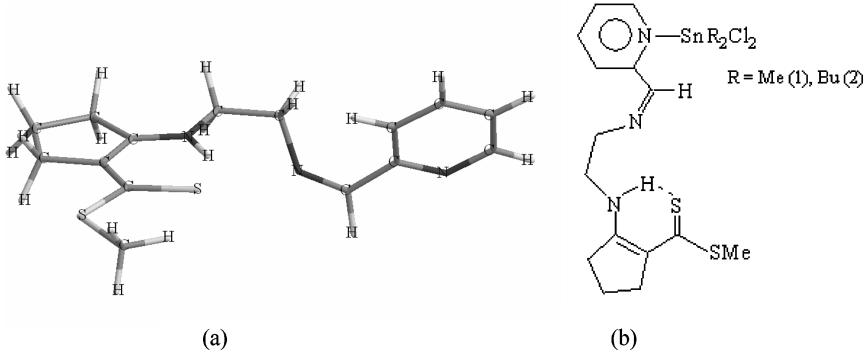


FIGURE 1 (a) Suggested structure for Hcdpen according to MP3 calculations and (b) structure of the organotin(IV) complexes **1** and **2.**

EXPERIMENTAL

All chemicals and solvents were purchased from commercial sources. Methyl-2-{*N*-(2′-aminoethane)}-amino-1-cyclopentenedithiocarboxylate (Hcden) was prepared by literature methods.[27,28] IR spectra were obtained using a FT BOMEM MB102 spectrophotometer. The ^{1}H and ^{119}Sn NMR spectra were recorded with a Brucker Avance DPZ500 spectrometer at 500.130 MHz and 186.496 MHz using TMS and $SnMe_4$ as references, respectively. The C, H, and N analyses were performed by the microanalytical service of the N.I.O.C. Research Institute of Petroleum Industry.

Synthesis of the Schiff Base

Pyridine 2-carbaldehyde (0.214 g, 2 mmol) was added to a solution of Hcden (0.433 g, 2 mmol) in methanol (10 mL). The solution was stirred at 38–40°C for 3 h. The red-brown reaction solution was cooled with an ice bath. The resulting yellow product was filtered, washed with cooled methanol (5 mL), and dried in vacuum over $CaCl_2$. Yield: 0.427 g (70%); m.p. 86–88°C; Anal. Calcd. for $C_{15}H_{19}N_3S_2$: C, 59.0; H, 6.2; N, 13.7%. Found: C, 58.7; H, 6.0; N, 13.5%. FT-IR (KBr, cm^{-1}): 1643, 1595, 1479, 1434, 1045, 615, 406. ^{1}H NMR ($CDCl_3$): $\delta = 1.86$ (m, 2H), 2.54 (s, 3H), 2.68–2.81 (m, 4H), 3.77 (m, 2H), 3.92 (t, $J = 6$ Hz, 2H), 7.34 (t, $J = 8$ Hz, 1H), 7.78 (t, $J = 7.6$ Hz, 1H), 7.99 (d, $J = 7.6$ Hz, 1H), 8.44 (s, 1H, HC=N), 8.66 (d, $J = 4.4$ Hz, 1H), 12.39 (s, 1H, NH).

Synthesis of [$SnMe_2Cl_2$(Hcdpen)] (1)

[$SnMe_2Cl_2$(Hcdpen)] (**1**) was synthesized by stirring $SnMe_2Cl_2$(0.37 g, 1.67 mmol) with Hcdpen (0.51 g, 1.67 mmol) in benzene (40 mL) solution at room temperature. An orange precipitate was formed after a few minutes. The mixture was stirred for 2 h at room temperature to ensure completion of the reaction. The product was filtered, washed with benzene (10 mL), and dried. Yield: 0.650 g (75%); m.p. 125–127°C (dec.); Anal. Calcd. for $C_{17}H_{25}N_3S_2Cl_2Sn$: C, 38.8; H, 4.8; N, 8.0%. Found: C, 39.1; H, 5.0; N, 7.7%. FT-IR (KBr, cm^{-1}): 1644, 1595, 1479, 1441, 1040, 636, 420. ^{1}H NMR ($CDCl_3$): $\delta = 1.11$ (s, $^{2}J(^{117/119}Sn\text{-}^{1}H) = 93.0/96.9$ Hz, 6H), 1.90 (m, 2H), 2.53 (s, 3H), 2.76 (t, $J = 6.4$ Hz, 2H), 2.80 (t, $J = 6.4$ Hz, 2H), 3.99 (m, 2H), 4.13 (t, $J = 4.3$ Hz, 2H), 7.62 (m, 1H), 7.95 (d, $J = 6.0$ Hz, 1H), 8.04 (m, 1H), 8.55 (s, 1H, HC=N), 9.11 (d, $J = 4.0$ Hz, 1H), 12.23 (s, 1H, NH). ^{119}Sn NMR ($CDCl_3$): $\delta = -89.5$.

Synthesis of [$SnBu_2Cl_2$(Hcdpen)] (2)

Complex **2** was synthesized as described for compound **1** from $SnBu_2Cl_2$ (0.51 g, 1.67 mmol) and Hcdpen (0.51 g, 1.67 mmol). Yield: 0.92 g (90%); m.p. 130–132°C (dec.); Anal. Calcd. for $C_{23}H_{37}N_3S_2Cl_2Sn$: C, 45.3; H, 6.1; N, 6.9%. Found: C, 45.4; H, 6.1; N, 6.9%. FT-IR (KBr, cm^{-1}): 1645, 1594, 1493, 1441, 1040, 637, 421. ^1H NMR ($CDCl_3$): $\delta = 0.82$ (t, $J = 5.7$ Hz, 6H), 1.26 (m, 4H), 1.51 (m, 4H), 1.61 (t, $J = 6.0$ Hz, 4H), 1.90 (m, 2H), 2.53 (s, 3H), 2.75–2.81 (m, 4H), 3.95 (m, 2H), 4.10 (t, $J = 4.0$ Hz, 2H), 7.57 (m, 1H), 7.95 (d, $J = 6.0$ Hz, 1H), 8.01 (t, $J = 6.0$ Hz, 1H), 8.55 (s, 1H), 9.03 (d, $J = 4.0$ Hz, 1H), 12.23 (s, 1H). ^{119}Sn NMR ($CDCl_3$): $\delta = -110.8$.

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