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New Adducts of Diorganotin(IV) Chlorides with a New Multifunctional Schiff Base Ligand: Synthesis and Spectral Properties

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Three novel Schiff base adducts $[SnMe_2Cl_2(Hcdacacen)]$ (**1**), $[SnBu_2Cl_2(Hcdacacen)_2]$ (**2**) and $[SnPh_2Cl_2(Hcdacacen)_2]$ (**3**) have been synthesized by reaction of SnR_2Cl_2 (R = Me, Bu and Ph) with a new Schiff base ligand methyl-2-[2-(acetylacetoneimino)ethylamino]-1-cyclopentene-1-dithiocarboxylate (Hcdacacen). The ligand and complexes were characterized by elemental analysis and spectroscopic studies. Spectroscopic data suggest that Hcdacacen exists predominately in ketamine tautomeric form and in all complexes acts as a monodentate neutral ligand coordinates to the metal through oxygen atom, while the sulfur atom and imine nitrogen is not involved in the coordination to the tin.

Keywords: Organotin(IV), Schiff base, Tautomeric forms, Tin(IV)

INTRODUCTION

The Schiff bases are among the most widely used ligands due to their facile synthesis, remarkable versatility and good solubility in common solvents. Thus, they have played an important role in the development of coordination chemistry as they readily form stable complexes with most of metals. The research field dealing with Schiff base metal complexes is very broad due to their potential interest for a number of interdisciplinary areas including bioinorganic chemistry, catalysis and magnetochemistry. In the area of bioinorganic chemistry, the interest in the Schiff base complexes lies in that they provide synthetic models for the metal containing sites in metalloproteins and enzymes [1].

Over the recent decades, studies on the organotin(IV) complexes with Schiff base ligands have received considerable attention. Organotin(IV) complexes have played an important role in medicine, agriculture and industry. Up to now, considerable efforts have been made to synthesize and characterize organotin compounds of ligands having heterodonor atoms (O, N, S), and many studies have been focused on their structure–activity correlations [2]. Many organotin(IV) compounds have been synthesized and tested for their antitumor activity and found to be as effective as, or even better than, traditional heavy anticancer drugs [3].

An interesting work in the field of bioinorganotin chemistry is the introduction ligands which are themselves bioactive [4]. Schiff bases are potential anticancer drugs and when administered as their metal complexes, the anticancer activity of these complexes is enhanced in comparison to the free ligand [5]. Therefore, organotin(IV) complexes of Schiff bases have received considerable attention with respect to their potential applications in medicinal chemistry and biotechnology [6]. Furthermore, organotin(IV) complexes with Schiff bases present an interesting variety of structural possibilities. This aspect has been attracting the attention of a number of researchers and a multitude of structural types have been discovered. Both aliphatic and aromatic Schiff bases in

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their neutral and deprotonated forms have been used to react with organotin(IV) halides; the complexes formed exhibit variable stoichiometry in the metal to ligand ratio and different modes of coordination [7].

In continuing our previous studies on the synthesis and characterization of organotin(IV) complexes, here we report the synthesis and characterization of novel complexes of diorganotin(IV) dichlorides with a new unsymmetrical Schiff base ligand, methyl-2-[2-(acetylacetoneimino)ethylamino]-1-cyclopentene-1-dithiocarboxylate (Hcdacacen) as a conformationally flexible ligand containing both hard and soft donor atoms O, N and S.

EXPERIMENTAL

Materials and Methods

All chemicals and solvents were purchased from commercial sources. Methyl-2-{*N*-(2′-aminoethane)}-amino-1-cyclopentenedithiocarboxylate (Hcden) was prepared by literature methods [8,9]. IR spectra were obtained using a FT BOMEM MB102 spectrophotometer. The ^{1}H and ^{119}Sn NMR spectra were recorded on a Brucker Avance DPZ500 spectrometer at 500.130 MHz and 186.496 MHz, respectively, using TMS and $SnMe_4$, as references. The CHN analyses were performed by the microanalytical service of the N.I.O.C. Research Institute of Petroleum Industry.

Synthesis of the Schiff Base

Acetylacetone (1.2 ml, 12 mmol) was added dropwise to a solution of Hcden (2.60 g, 12 mmol) in methanol (50 ml). This solution was stirred for 1 h at r.t. Then the resulting yellow product was filtered, washed with methanol (2 × 10 ml) and dried in vacuum over $CaCl_2$. Yield: 2.57 g (72%); m.p.: 128-130 °C; Anal. Calcd. for $C_{14}H_{22}N_2OS_2$: C, 56.37; H, 7.40; N, 9.40%. Found: C, 56.23; H, 7.70; N, 9.48 %. FT-IR (KBr, cm^{-1}): ν(NH) and ν(CH), 2800-3000; ν (CO), 1563. ^{1}H NMR ($CDCl_3$): δ = 1.88 (m, 2H), 1.95 (s, 3H), 2.03 (s, 3H), 2.58 (s, 3H), 2.68 (t, J = 7.7 Hz, 2H), 2.80 (t, J = 6.8 Hz, 2H), 3.55 (m, 4H), 5.00 (s, 1H), 10.94 (s, br, 1H), 12.41 (s, br, 1H).

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

[$SnMe_2Cl_2$(Hcdacacen)] (**1**) was synthesized by stirring $SnMe_2Cl_2$ (0.37 g, 1.67 mmol) with Hcdacacen (0.50 g, 1.67 mmol) in benzene (50 ml) solution at room temperature for 24 h. Then the solvent was evaporated and yellow precipitate was collected, washed with benzene (2 × 5 ml) and dried over $CaCl_2$. Yield: 0.55 g (63.7%); m.p.: 120 °C (dec.); Anal. Calcd. for $C_{16}H_{28}N_2OS_2Cl_2Sn$: C, 37.09; H, 5.41; N, 5.41%. Found: C, 37.22; H, 5.30; N, 5.71%. FT-IR (KBr, cm^{-1}): ν(NH), 3082; ν (CO), 1541; ν_{as}(Sn-C), 570; ν_s(Sn-C), 548; ν(Sn-O), 420. ^{1}H NMR ($CDCl_3$): δ = 1.21 (s, $^{2}J(^{119}Sn\text{-}^{1}H)$ = 76.5 Hz, 6H), 1.83 (m, 2H), 1.98 (s, 3H), 1.99 (s, 3H), 2.56 (s, 3H), 2.68 (t, J = 7.5 Hz, 2H), 2.79 (t, J = 7.0 Hz, 2H), 3.60 (m, 4H), 5.00 (s, 1H), 10.95 (s, br, 1H), 12.38 (s, br, 1H). ^{119}Sn NMR ($CDCl_3$): δ = 9.5.

Synthesis of [$SnBu_2Cl_2$(Hcdacacen)$_2$] (2)

A solution of Hcdacacen (0.99 g, 3.34 mmol) in benzene (20 ml) was added to a solution of $SnBu_2Cl_2$ (0.50 g, 1.67 mmol) in benzene (20 ml). The mixture was stirred for 2 h in r.t. During this period, the yellow precipitate was formed. The product was filtered, washed with benzene (2 × 10 ml) and dried over $CaCl_2$. Yield: 0.44 g (63.7%); m.p.: 131 °C (dec.); Anal. Calcd. for $C_{36}H_{62}N_4O_2S_4Cl_2Sn$: C, 45.15; H, 6.50; N, 5.85 %. Found: C, 45.12; H, 6.80; N, 5.53%. FT-IR (KBr, cm^{-1}): ν(NH), 3180; ν (CO), 1538; ν(Sn-O), 409. ^{1}H NMR ($CDCl_3$): δ = 0.94 (t, J = 7.2 Hz, 6H), 1.42 (m, 4H), 1.82 (m, 12H), 1.99 (s, 6H), 2.05 (s, 6H), 2.58 (s, 6H), 2.69 (t, J = 7.1 Hz, 4H), 2.81 (t, J = 7.0 Hz, 4H), 3.59 (m, 8H), 5.01 (s, 2H), 10.92 (s, br, 2H), 12.40 (s, br, 2H). ^{119}Sn NMR ($CDCl_3$): δ = 70.6.

This compound was also obtained from a 1:1 molar mixture of reagents.

Synthesis of [$SnPh_2Cl_2$(Hcdacacen)$_2$] (3)

Complex **3** was synthesized as described for compound **2** from $SnPh_2Cl_2$ (0.57 g, 1.67 mmol) and the yellow precipitate was collected after 4 h. Yield: 1.1 g (71%); m.p.: 80 °C (dec.); Anal. Calcd. for $C_{40}H_{54}N_4O_2S_4Cl_2Sn$: C, 51.08; H, 5.75; N, 5.96%. Found: C, 51.01; H, 5.43; N, 5.86%. FT-IR (KBr, cm^{-1}): ν(NH), 3185; ν (CO), 1536; ν(Sn-O), 414. ^{1}H NMR ($CDCl_3$): δ = 1.83 (m, 4H), 1.93 (s, 6H), 1.99 (s, 6H), 2.60 (s, 6H), 2.66 (t, J = 7.3 Hz, 4H), 2.81 (t, J = 7.5 Hz, 4H), 3.53 (m, 8H), 5.03 (s, 2H), 7.49-7.50 (m, 6H), 7.79 (d, J = 1.8 Hz, 4H, $^{3}J(^{119}Sn\text{-}^{1}H)$ = 93 Hz), 10.98 (s, br, 2H), 12.39 (s, br, 2H). ^{119}Sn NMR ($CDCl_3$): δ = -141.8.

This compound was also obtained from a 1:1 molar mixture of reagents.

RESULTS AND DISCUSSION

The Schiff base used in this work, methyl-2-[2-(acetylacetoneimino)ethylamino]-1-cyclopentene-1-dithiocarboxylate (Hcdacacen), is synthesized from the reaction of methyl-2-{*N*-(2′-aminoethane)}-amino-1-cyclopentenedithiocarboxylate (Hcden) with acetylacetone. In this reaction, only 1:1 condensation was occurred even when an excess of the amine was used. Structural formula for this Schiff base is given in Fig. 1; the forms I-III may be present in tautomeric equilibrium as shown. Condensation products of acetylacetone (2,4-pentanedione) and related β-diketones with mono and diamines have been the subjects of a variety of studies. Paramount in the consideration of these Schiff bases are questions of the positions of the keto-enol or amine-imine equilibrium and nature of the hydrogen bond in the six-membered chelate ring. It was shown earlier that, in common solvents, bis(acetylacetone)ethylenediimine and related Schiff bases exist in appreciable amounts in the ketoenamine (ketamine) form III [10,11].

The new complexes were prepared by reaction of SnR_2Cl_2 (R = Me, Bu and Ph) with Hcdacacen in benzene. The composition of the new compounds was confirmed by their analytical data and the suggested structures were recognized by spectroscopic investigations.

IR Spectra

In the IR spectrum of Schiff base the absence of a band in the free C=O stretching region (1700-1770 cm^{-1}) rules out a ketimine form I for Hcdacacen. There is no band in the range of 1610-1640 cm^{-1} attributable to C=N stretching vibration in form I or II. The band observed in 1562 cm^{-1} has been assigned as a perturbed carbonyl stretching with the frequency lowering from a free carbonyl ascribed to conjugation and hydrogen bonding in ketoenamine form III [10]. In the IR spectra of complexes, this band shifts to a lower frequency at ~1540 cm^{-1} providing evidence of participation of oxygen in bonding with tin and so weakening of C=O bond.

In the infrared spectrum of free ligand, no band is observed in the region 3200-3500 cm^{-1} attributable to the stretching vibration of the free NH or OH, indicating the intramolecular hydrogen bonding in ligand. Instead, these bands shift to lower frequencies and overlap with the ν(C-H) in the range of 2800-3000 cm^{-1}. In the IR spectra of organotin(IV) complexes a new band is appeared above 3000 cm^{-1} attributed to the stretching vibration of NH in acetylacetone moiety. This is due to the coordination of oxygen atom with tin, which weakens the hydrogen bonding and so causing more transferring of proton to nitrogen. However, the position of this band indicates that a ring is formed by the intramolecular hydrogen bond in the ligand is retained in adducts.

The appearance of new bands in the IR spectra of the synthesized complexes in the region 410-420 cm^{-1}, which may be assigned to ν(Sn-O), supports the bonding of oxygen to the tin atom [12-14]. The presence of both ν_s(Sn-C) and ν_{as}(Sn-C) in the IR spectrum of **1** is consistent with a nonlinear C-Sn-C configuration.

^{1}H NMR Spectra

In ^{1}H NMR spectrum of Hcdacacen, two bands at 1.95 and 2.03 ppm are due to the slightly non-equivalent methyl groups in the acetylacetone moiety. The presence of a signal at 5.0 ppm (1H) corresponds to the vinylic hydrogen and absence of a methylene signal near 3 ppm (2H) indicates no participation of ketimine form I in solution. The NH protons appear as two

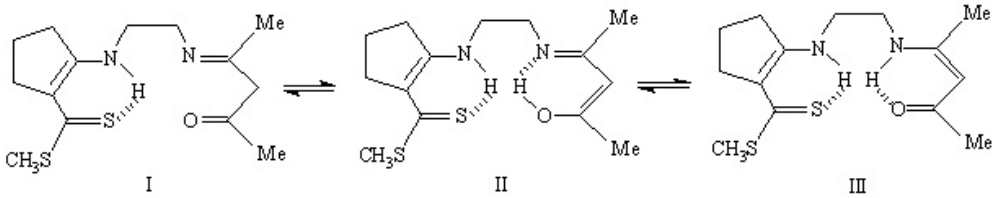

Fig. 1 Possible tautomeric forms for Hcdacacen.

broad signals at low field due to intramolecular hydrogen bonding. Broadening of the signal at 10.94 ppm, attributable to the NH proton in the acetylacetone moiety, indicates the weakening of the O-H bond and proton transfer to imine nitrogen atom (tautomeric form III) and, consequently, the interaction of the proton signal with the electric quadrupole moment of nitrogen [15,16].

In the ^{1}H NMR spectra of complexes, the ratio of the integrals of the signals of the ligand protons to those of the organic groups protons on tin provides a reliable measure of metal to ligand ratio in the synthesized complexes. The presence of both NH protons in ^{1}H NMR spectra of the synthesized complexes indicates that the Schiff base is coordinated to tin in a neutral form. The ^{1}H NMR spectrum of **1** shows a singlet at 1.21 ppm for $SnMe_2$ protons accompanied by satellites due to ^{1}H-^{119}Sn coupling. $^{2}J(^{119}Sn\text{-}^{1}H)$ for this compound (76.5 Hz) is larger than original $SnMe_2Cl_2$ (68.7 Hz) and falls in the range for five-coordinated dimethyltin(IV) species [7a,17-19]. Substituation of $^{2}J(^{119}Sn\text{-}^{1}H)$ in the Lockhart-Manders equation (1) [19] gives a value of 126.6° for the Me-Sn-Me angle.

$$[Me-Sn-Me] = 0.0161 \times [^{2}J(^{119}Sn\text{-}^{1}H)]^{2} - 1.32 \times [^{2}J(^{119}Sn\text{-}^{1}H)] + 133.4 \quad (1)$$

The $^{2}J(^{119}Sn\text{-}^{1}H)$ value for **2** can not be extracted from the spectrum because of the complexity of the methylene multiplets.

The ^{1}H NMR spectrum of **3** shows a doublet at 7.79 ppm attributable to the $H_{2,6}$ of Ph_2Sn moiety. This signal has ^{119}Sn satellites with $^{3}J(^{119}Sn\text{-}^{1}H)$ larger than uncomplexed $SnPh_2Cl_2$ (81.7 Hz). Generally, upon complexation, the magnitude of $J(^{119}Sn\text{-}^{1}H)$ 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.

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 [20]. Moreover, the signal attributable to the imine proton (HC=N) in the spectra of complexes is not accompanied by ^{119}Sn satellites, revealing the fact that the corresponding nitrogen atom is not coordinated to tin(IV) [21].

^{119}Sn NMR Spectra

The ^{119}Sn{^{1}H}NMR spectra of the complexes show a sharp singlet at 9.5, 70.6 and -141.8 ppm for **1**, **2** and **3**, respectively. These resonances appear significantly at lower frequency than that of $SnMe_2Cl_2$ (+137 ppm), $SnBu_2Cl_2$ (+123 ppm) and $SnPh_2Cl_2$ (-27 ppm) [22-24]. A very important property of ^{119}Sn NMR is that the corresonding chemical shift is strongly dependent on the coordination number of tin atom, and an increase in coordination number produces a large upfield shift. It has been shown that the $\delta(^{119}Sn)$ moves upfield by 60-150 ppm with a change in coordination number of tin from 4 to 5 and by 130-200 ppm from 5 to 6 [25-27]. On the basis of these chemical shift ranges, it appears reasonable to assume that for complex **1** the coordination number of the tin atom is five in solution. However the ^{119}Sn signal for **2** and **3** lie at higher frequencies than that for six-coordinate complexes of phenyltin and butyltin derivatives. This observation suggest that, in chloroform solution, the adduct partially dissociates and loses the six coordination structure, even though the presence of only one set of signals for the ligand in ^{1}H NMR spectrum of complexes indicates that the free and coordinated ligands are involved in a fast interchange [28].

In conclusion, in all complexes, Hcdacacen seems to act as a monodentate neutral ligand and coordinates to the metal as dangling form through oxygen atom while an intramolecular hydrogen bond still exists between O and N (Fig. 2).

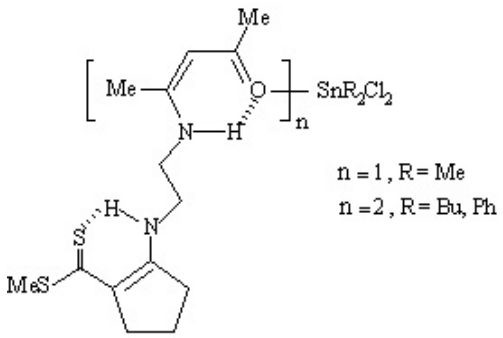

Fig. 2. Structure suggested for the coordination of Hcdacacen to Sn(IV).

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