Research Article

Synthesis and Characterization of New Lead(II) and Organotin(IV) Complexes of Schiff Bases Derived from Histidine and Methionine

Har Lal Singh and J. B. Singh
Department of Chemistry, Faculty of Engineering & Technology, Mody Institute of Technology and Science, Lakshmangarh, Rajasthan, Sikar 332311, India

Correspondence should be addressed to Har Lal Singh, hlsingh9@rediffmail.com

Received 29 November 2011; Accepted 17 January 2012

Academic Editor: Alfonso Castañeiras

Copyright © 2012 H. L. Singh and J. B. Singh. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

New Schiff base (HL) ligand is prepared via condensation of isatin and amino acids in 1:1 molar ratio. Metal complexes are prepared and characterized by elemental analysis, molar conductance, electronic, infrared, and multinuclear magnetic resonance (1H NMR, 13C NMR, and 119Sn NMR). The analytical data showed that the ligand acts as bidentate toward metal ions via azomethine nitrogen and carboxylate oxygen by a stoichiometric reaction of metal : ligand (1 : 2) to form metal complexes (Pb(II)(L)2 and Bu2Sn(L)2, where L is the Schiff base ligands of histidine and methionine). The conductivity values between 15 and 25 Ω−1cm2 mol−1 in DMF imply the presence of nonelectrolyte species. On the basis of the above spectral studies, distorted octahedral and tetrahedral geometry have been proposed for the resulting organotin(IV) and lead(II) complexes.

1. Introduction

Metal Schiff-base complexes have continued to play the role of one of the most important stereochemical models in main group and transition metal coordination chemistry due to their preparative accessibility, diversity, and structural variability. In recent years, a number of Schiff bases have been reported to possess significant and diverse biological activities such as antifungal, analgesic, anti-inflammatory, antibacterial, antioxidant, antitumor, local anesthetic, and antimicrobial activities [1–6]. On the other hand, radicals retard the progress of many chronic diseases such as vascular diseases, oxidative stress responsible for DNA, protein and membrane damage, and some forms of cancer [7, 8].

During the last few decades, metal carboxylates have been the subject of extensive investigations because of their remarkable structural diversity [9, 10] as well as significant biological activity, for example, pesticidal, bactericidal, and antitumor agents [11, 12]. In continuation of recent reports from this laboratory on some amino acid Schiff base metal complex systems [13–16], the present studies, ligand (L1H–L4H) is obtained by the condensation reaction between amino acids (L-histidine, DL-methionine) and isatin, chloroisatin with this hope that it may provide us valuable theoretical information for exploring metal-based bacteriostatic and carcinostatic pharmaceuticals with high efficacy and low toxicity. In this effort, we have also introduced an azomethine (–C=N–) linkage with the concern that it may permit a notable variety in the remarkable chemistry and behavior of such compounds. The synthesized Schiff base derived compounds (L1H–L4H) have been exposed to act as bidentate towards Pb(II) and Sn(IV) metal atom solely through the azomethine nitrogen and carboxylate oxygen forming a stable five-member chelate ring. The structures of the ligands are shown in Figure 1.

2. Experimental

All chemicals used in the present work, namely, isatin, 5-chloroisatin, L-histidine, DL-methionine, and metal acetate were of analytical grade. Solvents used were dried and purified by standard methods, and moisture was excluded.
from the glass apparatus using CaCl₂ drying tubes. The melting points of the compounds were determined on a capillary melting point apparatus and were not corrected. The purity of the compounds was confirmed by thin layer chromatography using silica gel-G glass plates as the stationary phase and benzene and ethanol (9:1) as the mobile phase.

2.1. Analytical Methods and Spectral Measurements. Tin and lead were determined gravimetrically as tin oxide and lead sulphate, respectively. Nitrogen and sulfur were estimated by Kjeldahl’s and Messenger’s methods, respectively. Molar conductance measurements were made in anhydrous dimethylformamide at 35 ± 5°C using a Systronics conductivity bridge model 305. Molecular weight determinations were carried out by the Rast camphor method.

The electronic spectra of the ligands and their metal complexes were recorded in dry DMSO on a Thermoscientific, Double-beam spectrophotometer UV 1, in the range of 800–200 nm. Multinuclear NMR spectra were recorded in dry DMSO-d₆ as solvent. Chemical Shifts are given ppm (d) and elemental analysis (%) calcd. for C₁₄H₁₂N₄O₃:C, 59.15; H, 4.25; N, 19.71; found, C: 59.01; H, 4.22; N, 19.63; molecular weight: found, 287.84, calcd. 284.27. ¹H NMR (DMSO-d₆, δ ppm, 400 MHz): 12.55 (s, 1H, COOH), 4.61 (t, 1H, N–CH–), 2.31 (d, 2H, –CH₂), 7.08–7.80 (m, 6H, aromatic); ¹³C NMR (DMSO, δ ppm): 177.4 (COOH); 54.8 (CH), 32.6 (CH₂); 163.7 (C=N); 156.6 (C=O); 145.5, 139.3, 137.8, 133.8, 130.4, 129.5, 121.3, 120.5, 117.9 (aromatic carbons); UV-visible (λmax, nm): 215, 265, 380; Infrared (KBr, cm⁻¹): ν(C=N), 1620; ν(COOH), 3090–2740; ν(C=O), 1728; ν(NH), 3130.

2-(5-chloro-2-oxoindolin-3-ylideneamino)-3-(1H-imidazol-4-yl)propanoic acid (L₁H) was prepared by reacting 5-chloroisatin with histidine: colour, grey; yield, 91.0%; mp, 110–112° C using a Systronics conductivity bride model 305. Molecular weight: found, 287.84, calcd. 284.27. ¹H NMR (DMSO-d₆, δ ppm, 400 MHz): 178.5 (COOH); 30.7 (CH₂); 162.4 (C=O); 146.3, 140.5, 137.6, 134.3, 130.2, 129.1, 122.9, 120.5, 115.2 (aromatic carbons); UV-visible (λmax, nm): 220, 264, 385; Infrared (KBr, cm⁻¹): ν(C=N), 1625; ν(COOH), 3100–27140; ν(C=O), 1730, ν(NH), 3140.

4-(methylthio)-2-(2-oxoindolin-3-ylideneamino)butanoic acid (L²H) was prepared by reacting isatin with methionine: colour, dark brown; yield, 91.0%; mp, 110–112° C using a Systronics conductivity bride model 305. Molecular weight: found, 287.84, calcd. 284.27. ¹H NMR (DMSO-d₆, δ ppm, 400 MHz): 178.5 (COOH); 30.7 (CH₂); 162.4 (C=O); 146.3, 140.5, 137.6, 134.3, 130.2, 129.1, 122.9, 120.5, 115.2 (aromatic carbons); UV-visible (λmax, nm): 220, 264, 385; Infrared (KBr, cm⁻¹): ν(C=N), 1625; ν(COOH), 3100–27140; ν(C=O), 1730, ν(NH), 3140.

2-(5-chloro-2-oxoindolin-3-ylideneamino)-4-(methylthio)butanoic acid (L¹H) was prepared by reacting 5-chloroisatin with methionine: colour, brown; yield, 76.2%; mp, 136–138° C (d) and elemental analysis (%) calcd. for C₁₄H₁₂N₄O₃S: C, 56.22; H, 5.01; N, 10.05; S, 11.63; molecular weight: found, 278.33, calcd. 283.18. ¹H NMR (DMSO-d₆, δ ppm, 400 MHz): 177.4 (COOH); 54.8 (CH), 32.6 (CH₂); 163.7 (C=N); 156.6 (C=O); 145.5, 139.3, 137.8, 133.8, 130.4, 129.5, 121.3, 120.5, 117.9 (aromatic carbons); UV-visible (λmax, nm): 215, 265, 380; Infrared (KBr, cm⁻¹): ν(C=N), 1625; ν(COOH), 3090–2750; ν(C=O), 1720; ν(NH), 3132.
Syntheses of Lead(II) and Organotin(IV) Complexes. The complexes were prepared under anhydrous conditions by the slow addition of a dry, hot methanol solution of the lead(II) acetate and dibutyltin oxide in 1:2 molar ratio to a solution of the Schiff bases in absolute methanol and benzene. The mixture was refluxed with constant stirring, giving a clear solution in half an hour; refluxing was then continued for 6-7 hours. The water and acetic acid liberated in the reaction was removed azeotropically with solvent. Excess solvent was removed under reduced pressure, and the compound was dried under vacuum at 45 °C after repeated washing with dry cyclohexane. The compounds were purified by recrystallization from the same solvent. The purity of the compounds was checked by TLC using silica gel G as absorbent.

Compound Pb(L1)2 was prepared by reacting lead(II) acetate with ligand (L1): colour, brown; yield, 76.7%; mp, 158–160 °C and elemental analysis (%), calcld. for PbC_{28}H_{20}Cl_{2}N_{8}O_{6}: Pb, 26.77; C, 37.59; H, 2.91; N, 6.74; S, 7.72; found: Pb, 26.82; C, 37.30; H, 2.88; N, 6.65; S, 7.78; molecular weight: found, 846.13; calcld. 830.73. Molar conductance (DMF, 10^{-3}, \Omega^{-1}, mol^{-1}, cm^{2}): 18.35; 1H NMR (DMSO-d6, ppm): 4.78 (t, 1H, \text{–CH2}–), 2.29 (m, 4H, \text{–CH2}–). 8.12 (s, 1H, NH), 1.70 (s, 3H, CH3), 6.96–7.75 (m, 4H, aromatic); 13C NMR (DMSO, ppm), 185.3 (COO); 60.9 (CH2); 31.3 (CH2); 18.3 (CH3); 153.8 (C=N); 157.2 (C=O); 145.4, 136.1, 132.3, 129.4, 121.8, 118.5 (aromatic carbons); UV-visible (\lambda_{max}, nm): 212, 252, 375, 345; Infrared (KBr, cm^{-1}): \nu(C–N), 1725; \nu_{asym}(COO), 1585; \nu_{sym}(COO), 1318; \nu(Pb–N), 435; \nu(Pb–O), 565.

Compound Pb(L1)2 was prepared by reacting lead(II) acetate with ligand (L1): colour, brown; yield, 76.7%; mp, 158–160 °C and elemental analysis (%), calcld. for PbC_{28}H_{20}Cl_{2}N_{8}O_{6}: Pb, 26.77; C, 37.59; H, 2.91; N, 6.74; S, 7.72; found: Pb, 26.82; C, 37.30; H, 2.88; N, 6.65; S, 7.78; molecular weight: found, 846.13; calcld. 830.73. Molar conductance (DMF, 10^{-3}, \Omega^{-1}, mol^{-1}, cm^{2}): 18.35; 1H NMR (DMSO-d6, ppm): 4.78 (t, 1H, \text{–CH2}–), 2.29 (m, 4H, \text{–CH2}–). 8.12 (s, 1H, NH), 1.70 (s, 3H, CH3), 6.96–7.75 (m, 4H, aromatic); 13C NMR (DMSO, ppm), 185.3 (COO); 60.9 (CH2); 31.3 (CH2); 18.3 (CH3); 153.8 (C=N); 157.2 (C=O); 145.4, 136.1, 132.3, 129.4, 121.8, 118.5 (aromatic carbons); UV-visible (\lambda_{max}, nm): 212, 252, 375, 345; Infrared (KBr, cm^{-1}): \nu(C–N), 1725; \nu_{asym}(COO), 1585; \nu_{sym}(COO), 1318; \nu(Pb–N), 435; \nu(Pb–O), 565.
The chelates were dissolved in DMF, and molar conductance values of the complexes fall in the range 1600 ± 5 cm⁻¹ suggesting the involvement of the azomethine nitrogen with the Sn(IV) and Pb(II) ion [19–21]. The spectra of the ligands show a broad absorption band observed in the region 3100–2560 cm⁻¹ which is assigned to hydrogen bond ν(OH) [14]. This band disappears on complexation, suggesting the chelation of the oxygen to the metal atoms. The ν(COO)asym and ν(COO)sym stretching vibrations characteristic of the coordinated carboxylate anions were indicated as strong intensity bands near 1600 and 1330 cm⁻¹, respectively [22]. The observed large separation between νasym(COO) and νsym(COO) stretching vibrations [Δν = νasym (COO) − νsym(COO) ∼ 270 cm⁻¹] for carboxylate group show the bidentate nature of ligands in the complexes. However, in the case of the free ligands and complexes, a strong band present in the free carbonyl region 1740 ± 5 cm⁻¹ shows that in these complexes the carboxylate group is bonded to metal in a unidentate manner [23]. Appearance of a band at 3315–3350 cm⁻¹ in the spectra of ligands has been assigned to the stretching vibrations of the ν(N–H) groups, which remains unaltered in the metal complexes, indicating its noninvolvement in coordination.

These overall data suggest that the azomethine nitrogen and carboxylate oxygen groups are involved in coordination with the Bu₂Sn(IV) and Pb(II) ion in the complexes. Several new band appearing in the complexes at ~460, ~545, ~660, ~460, and ~540 cm⁻¹ are probably due to ν(Sn–O) [15, 24], ν(Sn–N) [15, 25], ν(Sn–C) [15, 26], ν(Pb–O) [13, 27], and ν(Pb–N) [13, 27], respectively.

3.2. Electronic Spectra. The spectra of the ligands and their metal complexes were recorded in dry DMSO. The various bands observed were assigned to interligand and charge transfer of n–π* transitions according to their energies and intensities. A band due to the C=N chromophore in the spectrum of ligand at ~380 nm (π–π* transition) shifts to a lower wavelength in the spectra of metal complexes and appears at ~372 nm in the complexes. This clearly indicates the coordination of azomethine nitrogen to the metal atom. Bands at higher energies (260–265 nm and 210–220 nm) are attributed to the indole ring π–π* and n–π* transition. The complexes also show one bands in the region 345–358 nm, and these may be assigned as charge transfer bands. It has been reported that the metal is capable of forming dπ–π* bonds with ligands containing nitrogen as the donor atom. The metal atom has its d orbital completely vacant, and hence M–N bonding can take place by the acceptance of the lone pair of electrons from the nitrogen of the ligands.

3. Results and Discussion

The Schiff base (HL) and metal complexes are subjected to elemental analysis. The results of elemental analysis (C, H, and N) with molecular formula and the melting points are presented in Section 2. The results obtained are in good agreement with those calculated for suggested formula. New metal complexes were synthesized by the reaction of dibutyltin(IV) oxide and lead(II) acetate with Schi bases being carried out in 1:2 molar ratios using anhydrous benzene and absolute methanol in 3:1 ratio as solvent. These reactions proceed with the liberation of water and acetic acid, which were azetropically removed. The scheme of the organotin(IV) and lead(II) complexes preparation is given by Scheme 1.

The above reactions were found to be quite facile and could be completed in 6–7 h of refluxing. The resulting complexes have been obtained as coloured solid which are soluble in methanol, dimethylformamide, and dimethylsulfoxide. The chelates were dissolved in DMF, and molar conductance of 10⁻³ M of this solution at 35 ± 5°C was measured. The molar conductance values of the complexes fall in the range 15 to 25 Ω⁻¹cm² mol⁻¹ indicating that these chelates are nonelectrolyte.

3.1. Infrared Spectra. The IR spectra of all the ligands show the absence of bands at 3250 and 1740 cm⁻¹ due to ν(NH₂) group of amino acids and ν(C=O) of isatin. Instead, a new prominent band at 1625 ± 5 cm⁻¹ due to azomethine ν(C=N) linkage appeared in all the ligands [17, 18] indicating that condensation between ketone moiety of isatin and that of amino group of amino acid has taken place resulting into the formation of the desired ligands (L¹H)–(L⁴H). Moreover, on comparison of the IR spectra of the ligands with their Bu₂Sn(IV) and Pb(II) complexes showed a major shift to lower wave numbers by 10–15 cm⁻¹ in azomethine ν(C=N) at 1610 ± 5 cm⁻¹ suggesting the involvement of the azomethine nitrogen with the Sn(IV) and Pb(II) ion [19–21]. The spectra of the ligands show a broad absorption band observed in the region 3100–2560 cm⁻¹ which is assigned to hydrogen bond ν(OH) [14]. This band disappears on complexation, suggesting the chelation of the oxygen to the metal atoms. The ν(COO)asym and ν(COO)sym stretching vibrations characteristic of the coordinated carboxylate anions were indicated as strong intensity bands near 1600 and 1330 cm⁻¹, respectively [22]. The observed large separation between νasym(COO) and νsym(COO) stretching vibrations [Δν = νasym (COO) − νsym(COO) ∼ 270 cm⁻¹] for carboxylate group show the bidentate nature of ligands in the complexes. However, in the case of the free ligands and complexes, a strong band present in the free carbonyl region 1740 ± 5 cm⁻¹ shows that in these complexes the carboxylate group is bonded to metal in a unidentate manner [23]. Appearance of a band at 3315–3350 cm⁻¹ in the spectra of ligands has been assigned to the stretching vibrations of the ν(N–H) groups, which remains unaltered in the metal complexes, indicating its noninvolvement in coordination.

These overall data suggest that the azomethine nitrogen and carboxylate oxygen groups are involved in coordination with the Bu₂Sn(IV) and Pb(II) ion in the complexes. Several new band appearing in the complexes at ~460, ~545, ~660, ~460, and ~540 cm⁻¹ are probably due to ν(Sn–O) [15, 24], ν(Sn–N) [15, 25], ν(Sn–C) [15, 26], ν(Pb–O) [13, 27], and ν(Pb–N) [13, 27], respectively.
Scheme 1: Representative equation illustrating the formation of Bu₂Sn(IV) and Pb(II) complexes.

\[
\begin{align*}
\text{Bu}_2\text{SnO} + 2\text{N} \overset{\text{1:2}}{\rightarrow} \text{Bu}_2\text{Sn(N} \overset{\text{O}}{\text{)}_2} + \text{H}_2\text{O} \\
\text{Pb(OOCCH}_3\text{)}_2 + 2\text{N} \overset{\text{1:2}}{\rightarrow} \text{Pb(N} \overset{\text{O}}{\text{)}_2} + 2\text{CH}_3\text{COOH}
\end{align*}
\]

where \(\text{N} \overset{\text{O}}{\text{)}\) represents the donor system of the Schiff bases.

Figure 2: Proposed structure of organotin(IV) and lead(II) complexes.

3.3. \(^1\text{H NMR Spectra.}\) The characteristic resonance peaks for the synthesized compounds have been recorded in DMSO-\(d_6\) and data are given in experimental section. The expected resonances are assigned by their peak multiplicity, intensity patterns, and integration. The integration peaks show good agreement with number of protons in the complexes. The \(^1\text{H NMR\) spectral data of the ligands show single resonance at \(\delta 12.15 \pm 0.40\) ppm, which is absent in the spectra of the complexes, indicating the replacement of the carboxylic acid proton by the organotin(IV) and lead(II) moiety. The ligands give a complex multiplet signal in the region \(\delta 6.95–7.82\) ppm for the aromatic protons, and these remain almost at the same position in the spectra of the metal complexes. The appearance of signals due to NH protons at the same positions in the ligand and its complexes show the noninvolvement of this group in coordination (Figure 2).

The complexes, however, show additional signals at \(\delta 0.72–1.90\) ppm owing to the protons of the butyl group. The \(\text{CH}_2(\alpha)\) protons of dibutyltin compounds are significant as a triplet at \(0.80\) ppm with \(^3\text{J}_{\text{HH}} = 7.4\) Hz, while \(-\text{CH}_2–\text{CH}_2–\) protons appear as a multiplet. Terminal protons of dibutyltin(IV) also show a triplet at \(0.98\) ppm with \(^3\text{J}_{\text{HH}} = 7.6\) Hz. The most important information obtained from \(^1\text{H NMR\) values in these compounds demonstrates that diorganotin complexes show the coordination number greater than four, probably six, in noncoordinating solvent.

3.4. \(^{13}\text{C NMR Spectra.}\) The \(^{13}\text{C NMR\) spectral data for ligands and their corresponding metal complexes have been recorded in Section 2. Evidence of the formation of the complexes is clearly displayed in the \(^{13}\text{C NMR\) spectra. The \(^{13}\text{C NMR\) spectra of complexes showed the \(\delta(\text{COO})\) signal shifted to the downfield region which is lower compared to that of the ligand (\(\sim \delta 177.8\) ppm) indicating the carboxylate anion is bonded to metal atom upon complexation.

The signals due to the carbon atom attached to the azomethine group in the ligands appear at \(\delta 160 \pm 2\) ppm. However, in the spectra of the corresponding metal complexes, these appear at \(\sim \delta 154.7\) ppm. The considerable shifts in the resonance of the carbon atom attached to nitrogen indicate the involvement of azomethine nitrogen atom in coordination. The occurrence of resonances in the range of \(\delta 115.5–145.8\) ppm in the \(^{13}\text{C NMR\) spectra of the complexes and ligand is defined as aromatic carbons signals. Generally, the \(^{13}\text{C NMR\) spectra of the complexes obtained were found to exhibit no additional resonances and thus reflects the purity of the complexes.

The carbon of the butyl group is observed at \(\sim \delta 26.6, 27.8, 26.0, 14.3\) ppm) position comparable to other similar compounds. The \(R\) group attached to tin displays resonance for chemically equivalent carbon; however, the butyl compounds display three resonances. Coordination of the tin atom has been related to \(^{1}J^{(119}\text{Sn–^{13}C}\) coupling constants. The \(^{1}J^{(119}\text{Sn–^{13}C}\) coupling constant values (\(n = 1, \sim 925\) Hz; \(n = 2, \sim 40\) Hz; \(n = 3, \sim 126\) Hz) obtained for the synthesized complexes are indicative of hexacoordination of dibutyltin complexes. The carbons of alkyl groups attached to tin are observed at position comparable with other similar compounds [28].

3.5. \(^{119}\text{Sn NMR Spectra.}\) The value of \(\delta^{(119}\text{Sn}\) defines the coordination number of the central tin atom. All the complexes, \(^{119}\text{Sn NMR\) spectra, show only a sharp singlet indicating the formation of a single species. For diorganotin(IV) complexes, the \(\delta^{(119}\text{Sn}\) value for four-coordinated complexes fall in the range between \(\delta +200\) and \(\delta –60\) ppm,
for five-coordinated complexes fall in the range between δ = 90 and δ = 190 ppm and for six-coordinated complexes fall in the range between δ = 210 and δ = 400 ppm. Schiff base derivatives of dibutyltin(IV) exhibited δ(119Sn) values at ~δ = 360 ppm which lie in the range of δ = 210 and δ = 400 ppm, hence indicating that the tin atom in all the complexes have six-coordinated and have a distorted octahedral geometry [29–31].

4. Conclusion

New Schiff base and their metal complexes have been successfully synthesized. Elemental analysis data obtained are in good agreement with the predicted formula. Distorted octahedral and tetrahedral geometries have been proposed for 1:2 organotin(IV) and lead(II) complexes with the help of various physicochemical studies. The infrared spectra of these complexes show the presence of monofunctional and bidentate ligands. The 1H NMR spectra showed that the calculated number of protons for each functional group in the complexes is equal to the number predicted from the molecular formula. Moreover, the 1H and 13C NMR spectra of the complexes obtained were found to exhibit no additional resonances, thus reflects the purity of the metal complexes.

Acknowledgments

The authors are thankful to the Dean, Faculty of Engineering & Technology, Mody Institute of Technology and Science, Deemed University, Lakshmangarh, Sikar, for providing necessary facilities and financial support. They are also thankful to the Head, SAIF, Panjab University, Chandigarh, for providing elemental analysis and NMR facilities.

References


Submit your manuscripts at http://www.hindawi.com