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Synthesis and characterization of Pb(II) complexes of Schiff bases derived from 3-methyl-4-fluoroacetophenone and amino acids

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Abstract A series of Pb(II) complexes of the type $Pb(L)_2$ have been synthesized with fluorinated Schiff bases derived from 3-methyl-4-fluoroacetophenone and amino acids (viz phenylalanine, alanine, tryptophan, valine, isoleucine, and glycine). These complexes are insoluble in common organic solvents but soluble in DMF and DMSO. The measured molar conductance values in DMF indicate that the complexes are non-electrolytes. On the basis of analytical and spectral (IR, UV–visible, and ^{1}H, ^{13}C and ^{19}F NMR) studies, it has been concluded that all the metal complexes have square planar geometry in which the ligand is coordinated to the metal ion through the azomethine nitrogen atom and the carboxylate oxygen atom via deprotonation.

Keywords Fluorinated Schiff bases · Lead(II) complexes · Spectral studies

Introduction

Metal carboxylates have been the subject of extensive investigations because of their remarkable structural diversity [1–3] and substantial biological activity, for examples as antimicrobial and antitumour agents [4–6]. In recent years, more and more investigations have focussed on the synthesis of metal carboxylates of functionalized carboxylic acids with additional oxygen [7, 8], sulfur [8, 9], or nitrogen [10–12] donor groups.

Amino acids, which constitute a very important class of biomolecules, can act as potential oxygen and nitrogen donor ligands. It has been found that they utilize their functional groups as fully as possible in metal coordination [12]. Therefore, several

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metal derivatives of different amino acids have been reported [13, 14] and some of these have been found to have significant biological activity, for example, tricyclohexyltin alaninate has been found to be active as a fungicide and bactericide for seeds and plants [15]. It has been reported that metal complexes of amino acid Schiff bases with transition metals have anticarcinogenic [16], antimicrobial [17] and antitumour [18] activity. Because its small size, fluorine has been used as a replacement for hydrogen in many biologically active molecules, including amino acids [19]. Once introduced, the strong carbon fluorine bond is particularly resistant to metabolic transformations, and the electronegativity of fluorine can have a substantial effect on the basicity or acidity of neighboring groups and on the electron distribution, and can change the overall reactivity and stability of a molecule [20]. Incorporation of fluorine into heterocycles is known to affect the course of their reactions and their biological activity [21]. It has been observed that introduction of a fluorine atom into heterocycles may act as a pharmocophore, enhancing the pharmacological properties of compounds compared with their non-fluorinated analogues [22].

This paper deals with the synthesis and characterization of lead complexes in order to study the mode of bonding of fluorinated ligands (Fig. 1). The ligands have C=N and COOH as the main donating groups. In this paper we examine the mode of bonding of these sites to the central metal ion and whether this takes place through nitrogen or oxygen, or both, donor atoms to confirm the bidentate nature of the ligands in these complexes. The structures of the ligands are shown in Fig. 1.

Experimental

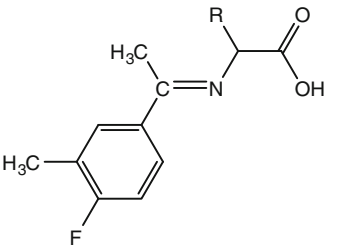
All chemicals used in this work, viz, 3-methyl-4-fluoroacetophenone, amino acids, and metal acetates, were of analytical grade. Solvents used were dried and purified by standard methods and moisture was excluded from glass apparatus by use of $CaCl_2$ drying tubes. Melting points were determined in an open glass capillary and were uncorrected.

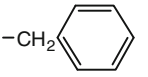
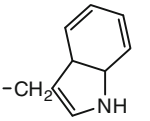
Preparation of the ligands

The ligands were synthesized by condensation of 3-methyl-4-fluoroacetophenone (0.601 g, 3.94 mmol) with the amino acids (phenylalanine alanine, tryptophan, isoleucine, valine, and glycine; 0.805–0.296 g, 3.94 mmol) in 1:1 molar ratio, using methanol (120 mL) as the reaction medium, under reflux for 6–8 h. After cooling at room temperature the solid products were obtained. The excess solvent was removed on a rotary evaporator. The residue was further dried and then purified by recrystallization from the same solvent.

L^1H was prepared by reacting 3-methyl-4-fluoroacetophenone with glycine, colour, yellow; yield, 70%; mp, 230 °C (d) and elemental analysis (%), calcd. for $C_{11}H_{12}FNO_2$: C, 63.15; H, 5.78; N, 6.69; found, C: 63.10; H, 5.71; N, 6.61; molecular weight: found, 201.63, calcd. 209.22. ^{1}H NMR (DMSO-d_6, δ ppm): 11.28

Fig. 1 Structures of the ligands



1a-f	R	Abbreviation
a	–H	L^1H
b	$-CH_3$	L^2H
c	$-CH(CH_3)_2$	L^3H
d	$-CH(CH_3)CH_2CH_3$	L^4H
e		L^5H
f		L^6H

(s, 1H, COOH), 4.20 (s, 2H, $–CH_2–$), 1.91 (s, 3H, $–C(CH_3)=N–$), 2.15 (s, 3H, $Ph–CH_3$), 6.99–7.20 (m, 3H, aromatic); ^{13}C NMR (DMSO, δ ppm): 175.9 (COOH), 63.6 ($–CH_2–$), 165.2 (C=N), 17.1 ($–CH_3$), 14.2 ($Ph–CH_3$), 137.2, 128.1, 119.9, 164.1, 121.8, 128.4 (Aromatic carbons); ^{19}F NMR (DMSO-d_6, δ ppm): −76.1; UV–visible (λmax, nm): 390, 214, 265; Infrared (KBr, cm^{-1}): ν(C=N), 1625; ν(COOH), 3100–2750; ν(C=O), 1715.

L^2H was prepared by reacting 3-methyl-4-fluoroacetophenone with valine, colour, light pink; yield, 78%; mp, 140 °C (d) and elemental analysis (%), calcd. for $C_{14}H_{18}FNO_2$: C, 66.91; H, 7.22; N, 5.57; found, C: 66.76; H, 7.10; N, 5.49; molecular weight: found, 240.09, calcd. 251.29. ^1H NMR (DMSO-d_6, δ ppm): 11.48 (s, 1H, COOH), 4.08 (d, 1H, NCH–C), 1.86 (s, 3H, $–C(CH_3)=N–$), 2.15 (s, 3H, $Ph–CH_3$), 1.07 (d, 3H, $–C–CH_3$), 2.39 (m, 1H, –CH–), 7.02–7.15 (m, 3H, aromatic); ^{13}C NMR (DMSO, δ ppm): 177.2 (COOH), 71.3 (N–CH–), 161.1 (C=N), 17.4 ($–CH_3$), 15.2 ($Ph–CH_3$), 33.2 (–CH–), 18.6 ($–CH_3$), 136.7, 128.3, 120.1, 164.3, 122.2, 129.6 (aromatic carbons); ^{19}F NMR (DMSO-d_6, δ ppm): −75.9; UV–visible (λmax, nm): 395, 205, 265; Infrared (KBr, cm^{-1}): ν(C=N), 1630; ν(COOH), 3090–2695; ν(C=O), 1710.

L^3H was prepared by reacting 3-methyl-4-fluoroacetophenone with alanine, colour, brown; yield, 72%; mp, 176 °C (d) and elemental analysis (%), calcd. for

$C_{12}H_{14}FNO_2$: C, 64.56; H, 6.32; N, 6.27; found, C: 64.36; H, 6.25; N, 6.18; molecular weight: found, 215.87, calcd. 223.24. ^{1}H NMR (DMSO-d_6, δ ppm): 11.68 (s, 1H, COOH), 4.56 (q, 1H, NCH–C), 1.89 (s, 3H, –C(CH_3)=N–), 2.24 (S, 3H, Ph–CH_3), 1.48 (d, 3H, –CH_3), 6.98–7.36 (m, 8H, aromatic); ^{13}C NMR (DMSO, δ ppm): 175.7 (COOH), 64.5 (N–CH–), 163.1 (C=N), 17.3 (–CH_3), 14.8 (Ph–CH_3), 18.6 (–CH_2–Ph), 136.4, 127.3, 120.1, 164.1, 120.1, 128.9 (aromatic carbons); ^{19}F NMR (DMSO-d_6, δ ppm): −76.7; UV–visible (λmax, nm): 392, 208, 264; Infrared (KBr, cm^{-1}): ν(C=N), 1620; ν(COOH), 3070–2590; ν(C=O), 1620.

L^4H was prepared by reacting 3-methyl-4-fluoroacetophenone with isoleucine: colour, light yellow; yield, 68%; mp, 244 °C (d) and elemental analysis (%), calcd. for $C_{15}H_{20}FNO_2$: C, 67.90; H, 7.60; N, 5.28; found, C: 67.82; H, 7.48; N, 5.22; molecular weight: found, 255.58, calcd. 265.32. ^{1}H NMR (DMSO-d_6, δ ppm): 11.59 (s, 1H, COOH), 4.51 (d, 1H, NCH–C), 1.56 (q, 2H, –CH_2–), 1.88 (s, 3H, –C(CH_3)=N–), 2.18 (s, 3H, Ph–CH_3), 1.27 (d, 3H, –C–CH_3), 0.98 (m, 1H, –C–CH–C), 7.00–7.19 (m, 3H, aromatic); ^{13}C NMR (DMSO, δ ppm): 178.2 (COOH), 66.7 (–CH_2–), 162.1 (C=N), 16.3 (–CH_3), 14.6 (Ph–CH_3), 36.5 (–CH_2–Ph), 136.9, 128.4, 119.1, 164.2, 122.2, 129.8,138.8, 128.4, 129.7, 116.7 (aromatic carbons); ^{19}F NMR (DMSO-d_6, δ ppm): −76.2; UV–visible (λmax, nm): 390, 210, 260; Infrared (KBr, cm^{-1}): ν(C=N), 1628; ν(COOH), 3100–2680; ν(C=O), 1724.

L^5H was prepared by reacting 3-methyl-4-fluoroacetophenone with phenylalanine: colour, Pink; yield, 75%; mp, 220 °C (d) and elemental analysis (%) calcd. for $C_{18}H_{18}FNO_2$: C, 72.22; H, 6.06; N, 4.68; found, C: 72.01; H, 6.00; N, 4.60; molecular weight: found, 286.44, calcd. 299.34. ^{1}H NMR (DMSO-d_6, δ ppm): 11.52 (s, 1H, COOH), 4.21 (t, 1H, NCH–C), 2.98 (d, 2H, –CH_2–), 1.82 (s, 3H, –C(CH_3)=N–), 2.09 (s, 3H, Ph–CH_3), 6.98–7.50 (m, 8H, aromatic); ^{13}C NMR (DMSO, δ ppm): 178.2 (COOH), 66.7 (–CH_2–), 162.1 (C=N), 16.3 (–CH_3), 14.6 (Ph–CH_3), 36.5 (–CH_2–Ph), 136.9, 128.4, 119.1, 164.2, 122.2, 129.8,138.8, 128.4, 129.7, 116.7 (aromatic carbons); ^{19}F NMR (DMSO-d_6, δ ppm): −76.3; UV–visible (λmax, nm): 390, 210, 260; Infrared (KBr, cm^{-1}): ν(C=N), 1622; ν(COOH), 3080–2640; ν(C=O), 1722.

L^6H was prepared by reacting 3-methyl-4-fluoroacetophenone with tryptophan: colour, brownish gray; yield, 82%; mp, 254 °C (d) and elemental analysis (%), calcd. for $C_{20}H_{19}FN_2O_2$: C, 70.99; H, 5.66; N, 8.28; found, C: 70.85; H, 5.54; N, 8.02; molecular weight: found, 328.20, calcd. 338.37. ^{1}H NMR (DMSO-d_6, δ ppm): 11.54 (s, 1H, COOH), 4.49 (t, 1H, NCH–C), 3.17 (d, 2H, –CH_2–) 1.93 (s, 3H, –C(CH_3)=N–), 2.18 (s, 3H, Ph–CH_3), 6.98-7.55 (m, 8H, aromatic); ^{13}C NMR (DMSO, δ ppm): 178.2 (COOH), 66.7 (–CH_2–), 162.1 (C=N), 16.3 (–CH_3), 14.6 (Ph–CH_3), 36.5 (–CH_2–Ph), 136.9, 128.4, 119.1, 164.2, 122.2, 129.8,138.8, 128.4, 129.7, 116.7 (aromatic carbons); ^{19}F NMR (DMSO-d_6, δ ppm): −76.4; UV–visible (λmax, nm): 388, 210, 262; Infrared (KBr, cm^{-1}): ν(C=N), 1625; ν(COOH), 3095–2710; ν(C=O), 1715.

Synthesis of lead(II) complexes

The complexes were prepared under anhydrous conditions by slow addition of a dry, hot methanol solution of lead(II) acetate in 1:2 molar ratio to a solution of the

Schiff base in hot absolute methanol. The mixture was heated under reflux with constant stirring for 30 min, giving a clear solution; heating under reflux was then continued for 4–5 h. The acetic acid librated in the reaction was removed azeotropically with solvent. Excess solvent was removed under reduced pressure and the compound was dried under vacuum at 45 ± 5 °C after repeated washing with dry cyclohexane. The compounds were purified by recrystallization from methanol. The purity of the compounds was checked by TLC using silica gel G as adsorbent.

$Pb(L^1)_2$ was prepared by reacting lead(II) acetate with ligand (L^1H); colour, cream; yield, 65%; and elemental analysis (%), calcd. for $PbC_{22}H_{22}F_2N_2O_4$: Pb, 33.22; C, 42.37; H, 3.56; N, 4.49; found: Pb, 33.10; C, 42.49; H, 3.69; N, 4.42; molecular weight: found, 608.85, calcd. 623.62. Molar conductance (DMF, 10^{-3}, Ω^{-1}, mol^{-1}, cm^2): 21.6; ^1H NMR (DMSO-d_6, δ ppm): 4.22 (s, 2H, –CH_2–), 2.04 (s, 3H, –C(CH_3)=N–), 2.13 (s, 3H, Ph–CH_3), 6.96–7.28 (m, 3H, aromatic); ^{13}C NMR (DMSO, δ ppm): 166.4 (COO), 64.1 (–CH_2–), 154.9 (C=N), 17.2 (–CH_3), 14.4 (Ph–CH_3), 136.8, 128.7, 120.9, 164.1, 121.2, 128.7 (aromatic carbons); ^{19}F NMR (DMSO-d_6, δ ppm): −72.1; UV–visible (λmax, nm): 380, 215, 268, 365; Infrared (KBr, cm^{-1}): ν(C=N), 1610; ν(C=O), 1712; ν_{asym}(COO), 1555; ν_{sym}(COO), 1310; ν(Pb ← N), 535; ν(Pb–O), 465.

$Pb(L^2)_2$ was prepared by reacting lead(II) acetate with ligand (L^2H): colour, light yellow; yield, 76%; mp, 158–159 °C and elemental analysis (%), calcd. for $PbC_{28}H_{34}F_2N_2O_4$: Pb, 29.27; C, 47.52; H, 5.84; N, 3.96; found; Pb, 29.36; C, 47.32; H, 5.73; N, 3.77; molecular weight: found, 692.50, calcd. 707.76. Molar conductance (DMF, 10^{-3}, Ω^{-1}, mol^{-1}, cm^2): 18.15; ^1H NMR (DMSO-d_6, δ ppm): 4.09 (d, 1H, NCH–C), 1.98 (s, 3H, -C(CH_3)=N–), 2.17 (s, 3H, Ph–CH_3), 1.09 (d, 3H, –C–CH_3), 2.45 (m, 1H, –CH–), 6.99–7.26 (m, 3H, aromatic); ^{13}C NMR (DMSO, δ ppm): 167.5 (COO), 71.3 (N–CH–), 152.8 (C=N), 17.6 (–CH_3), 15.1 (Ph–CH_3), 33.4 (–CH–), 18.5 (–CH_3), 136.6, 128.5, 120.3, 164.1, 121.9, 129.6 (aromatic carbons); ^{19}F NMR (DMSO-d_6, δ ppm): −72.4; UV–visible (λmax, nm): 385, 208, 260, 360; Infrared (KBr, cm^{-1}): ν(C=N), 1615; ν(C=O), 1712; ν_{asym}(COO), 1535; ν_{sym}(COO), 1306; ν(Pb ← N), 530; ν(Pb–O), 455.

$Pb(L^3)_2$ was prepared by reacting lead(II) acetate with ligand (L^3H): colour, light brown; yield, 73%; and elemental analysis (%), calcd. for $PbC_{24}H_{26}F_2N_2O_4$: Pb, 31.79; C, 44.23; H, 4.02; N, 4.30; found: Pb, 31.58, C, 44.15; H, 4.22; N, 4.18; molecular weight: found, 645.08, calcd. 651.66. Molar conductance (DMF, 10^{-3}, Ω^{-1}, mol^{-1}, cm^2): 17.55; ^1H NMR (DMSO-d_6, δ ppm): 4.66 (q, 1H, N–CH–C), 1.99 (s, 3H, –C(CH_3)=N–), 2.20 (s, 3H, Ph–CH_3), 1.52 (d, 3H, –C–CH_3), 6.96-7.30 (m, 3H, aromatic); ^{13}C NMR (DMSO, δ ppm): 165.7 (COO), 64.5 (N–CH–), 156.4 (C=N), 17.5 (–CH_3), 15.2 (Ph–CH_3), 18.7 (–CH_2–Ar), 136.5, 127.1, 120.4, 164.2, 121.1, 128.6 (aromatic carbons); ^{19}F NMR (DMSO-d_6, δ ppm): −72.6; UV–visible (λmax, nm): 378, 210, 260, 360; Infrared (KBr, cm^{-1}): ν(C=N), 1608; ν(C=O), 1715; ν_{asym}(COO), 1545; ν_{sym}(COO), 1300; ν(Pb ← N), 530; ν(Pb–O), 460.

$Pb(L^4)_2$ was prepared by reacting lead(II) acetate with ligand (L^4H): colour, white; yield, 70%; mp, 232 °C and elemental analysis (%), calcd. for $PbC_{30}H_{38}F_2N_2O_4$: Pb, 28.16; C, 48.97; H, 5.20; N, 3.81; found: Pb, 28.02; C, 48.71; H, 5.02; N, 3.72; molecular weight: found, 726.17, calcd. 735.82. Molar conductance (DMF, 10^{-3}, Ω^{-1}, mol^{-1}, cm^2): 16.39; ^1H NMR (DMSO-d_6, δ ppm):

4.55 (d, 1H, NCH–C), 1.55 (q, 2H, $–CH_2–$), 1.97 (s, 3H, $–C(CH_3)=N–$), 2.20 (s, 3H, $Ph–CH_3$), 1.28 (d, 3H, $–C–CH_3$), 1.08 (m, 1H, –C–CH–C), 7.00–7.25 (m, 3H, aromatic); ^{13}C NMR (DMSO, δ ppm): 167.6 (COO), 65.9 ($–CH_2–$), 155.3 (C=N), 16.2 ($–CH_3$), 15.2 ($Ph–CH_3$), 36.8 ($–CH_2–Ph$), 136.9, 128.6, 119.7, 163.8, 123.1, 129.1,136.8, 128.5, 129.2, 118.2 (aromatic carbons); ^{19}F NMR (DMSO-d_6, δ ppm): −70.3; UV–visible (λmax, nm): 382, 210, 266, 366; Infrared (KBr, cm^{-1}): ν(C=N), 1610; ν(C=O), 1720; ν_{asym}(COO), 1540; ν_{sym}(COO), 1310; ν(Pb ← N), 550; ν(Pb–O), 450.

Pb(L^5)$_2$ was prepared by reacting lead(II) acetate with ligand (L^5H): colour, cream; yield, 69%; and elemental analysis (%) calcd. for $PbC_{36}H_{34}F_2N_2O_4$: Pb, 25.77; C, 53.79; H, 4.26; N, 3.48; found: Pb, 25.60; C, 53.68; H, 4.18; N, 3.38; molecular weight: found, 791.89, calcd. 803.86. Molar conductance (DMF, 10^{-3}, Ω^{-1}, mol^{-1}, cm^2): 18.75; ^{1}H NMR (DMSO-d_6, δ ppm): 4.24 (t, 1H, NCH–C), 2.92 (d, 2H, $–CH_2–$), 1.96 (s, 3H, $–C(CH_3)=N–$), 2.19 (s, 3H, $Ph–CH_3$), 6.94–7.56 (m, 8H, aromatic); ^{13}C NMR (DMSO, δ ppm): 169.3 (COO), 66.6 ($–CH_2–$), 153.7 (C=N), 16.6 ($–CH_3$), 14.9 ($Ph–CH_3$), 35.5 ($–CH_2–Ph$), 135.1, 128.6, 120.1, 163.9, 124.3, 128.8,136.7, 128.4, 129.3, 117.5 (aromatic carbons); ^{19}F NMR (DMSO-d_6, δ ppm): −71.9; UV–visible (λmax, nm): 380, 210, 260, 368; Infrared (KBr, cm^{-1}): ν(C=N), 1605; ν(C=O), 1725; ν_{asym}(COO), 1545; ν_{sym}(COO), 1305; ν(Pb ← N), 540; ν(Pb–O), 450.

Pb(L^6)$_2$ was prepared by reacting lead(II) acetate with ligand (L^6H), Colour, yellow; yield, 81%; mp, 222 °C and elemental analysis (%), calcd. for $PbC_{40}H_{36}F_2N_4O_4$: Pb, 23.49; C, 54.58; H, 4.11; N, 6.35; found; Pb, 23.40; C, 55.14; H, 4.01; N, 6.19; molecular weight: found, 872.25, calcd. 881.92. Molar conductance (DMF, 10^{-3}, Ω^{-1}, mol^{-1}, cm^2): 18.05; ^{1}H NMR (DMSO-d_6, δ ppm): 4.52 (t, 1H, N–CH–C), 3.20 (d, 2H, $–CH_2–$) 20.6 (s, 3H, $–C(CH_3)=N–$), 2.15 (s, 3H, $Ph–CH_3$), 6.94–7.60 (m, 8H, aromatic); ^{13}C NMR (DMSO, δ ppm): 166.1 (COO), 66.3 ($–CH_2–$), 156.7 (C=N), 17.4 ($–CH_3$), 15.6 ($Ph–CH_3$), 37.1 ($–CH_2–Ph$), 135.8, 129.1, 119.7, 164.3, 122.9, 128.3,137.8, 129.1, 129.3, 116.5 (aromatic carbons); ^{19}F NMR (DMSO-d_6, δ ppm): −71.8; UV–visible (λmax, nm): 375, 215, 260, 363; Infrared (KBr, cm^{-1}): ν(C=N), 1610; ν(C=O), 1715; ν_{asym}(COO), 1550; ν_{sym}(COO), 1310; ν(Pb ← N), 555; ν(Pb–O), 460.

Analytical methods and spectral measurements

Lead was determined gravimetrically as lead sulfate. Nitrogen was determined by Kjeldahl's method. Molar conductance measurements were made in anhydrous dimethylformamide at 45 ± 5 °C using a Systronics model 305 conductivity bridge. Molecular weight determinations were carried out by the Rast camphor method.

Electronic spectra were recorded in DMSO on a Thermo spectrophotometer. Infrared spectra were recorded on a Perkin–Elmer RX1 FT–IR spectrophotometer in the region 4,000–400 cm^{-1}. ^{1}H NMR and ^{19}F NMR were recorded on a Jeol (model FX 90Q) using DMSO-d_6 as solvent at 89.55 MHz and 84.25 MHz, respectively. ^{13}C NMR was recorded on a 90 MHz Jeol (FX 90Q) NMR spectrometer using dry

DMSO as the solvent at 84.25 MHz. TMS was used as internal reference for ^{1}H NMR and ^{13}C NMR and hexafluorobenzene as external reference for ^{19}F NMR.

Results and discussion

Several new lead–Schiff base complexes were synthesized by reaction of lead(II) acetate with the ligands in 1:2 molar ratios using anhydrous benzene and absolute methanol in 3:1 ratio as solvent. These reactions proceed with the liberation of acetic acid, which was azeotropically removed, are indicated below (Scheme 1):

The reactions were found to be quite facile and could be completed after reflux for 5–7 h. All the complexes were intensely coloured solids. They are insoluble in common organic solvents and only soluble in DMF and DMSO. The chelates were dissolved in DMF and the molar conductance of 10^{-3} M solution at 45 °C was measured. The molar conductance valves of the complexes fall in the range 15–20 Ω^{-1} cm^2 mol^{-1} indicating that these chelates are non-electrolytes. The elemental analysis results (Experimental section) agree with the formulae proposed for the ligands and also confirmed the $Pb(L)_2$ (Fig. 2) composition of the Pb(II) chelates.

$$Pb(OOCCH_3)_2 \quad + \quad 2\overset{\frown}{N\ OH} \longrightarrow Pb(\overset{\frown}{N\ O})_2 + 2CH_3COOH$$

where $\overset{\frown}{N\ OH}$ represents the donor system of the Schiff bases

Scheme 1 Representative equation illustrating the formation of Pb(II) complexes

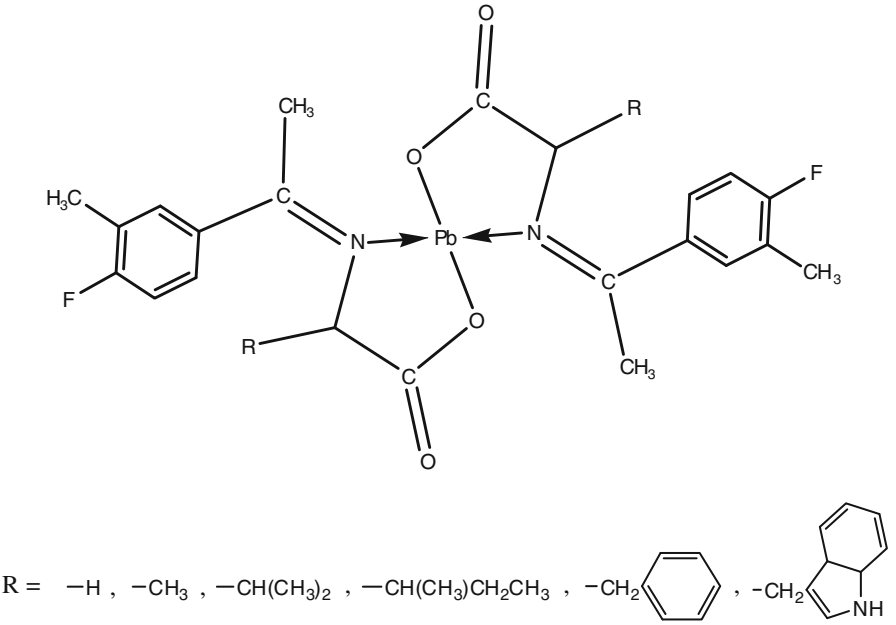


Fig. 2 Structures of the lead(II) complexes

Electronic spectra

The spectra of the ligands and their 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 at $\sim$390 nm due to the >C=N– chromophore in the spectrum of ligand (π–π^* transition) shifts to a lower wavelength and appears at 375 nm in the spectra of the lead complexes. This clearly indicates the coordination of the azomethine nitrogen to the lead atom. It was found that the electronic spectra of these complexes have very intense bands in the range 205–215 nm, which may be due to the n–π^* transition of the carboxylate chromophore [23]. The spectra of the complexes also have a few sharp bands in the region 240–265 nm, with one more band at $\sim$362 nm; these may be assigned as charge transfer bands. It has been reported that the metal is capable of forming dπ–pπ^* bonds with ligands containing nitrogen as the donor atom.

IR spectra

The important frequencies observed in FT–IR spectra of the compounds with their assignments are given in the Experimental section. The IR spectra of the complexes were compared with those of the free ligands in order to determine the coordination sites that may be involved in chelation. The position and the intensities of these peaks are expected to be changed on chelation. New peaks and quasi-peaks are also a guide to chelation. Moreover, comparison of the IR spectra of the ligands with those of their lead(II) complexes revealed [24] a major shift to lower wave numbers by 10–16 cm^{-1} in azomethine [24–26] ν(C=N) at 1610–1618 cm^{-1} suggesting involvement of the azomethine nitrogen with the Pb(II) ion. The spectra of the ligands contain a broad absorption band in the region 3,100–2,560 cm^{-1} which is assigned to hydrogen-bonded ν(OH) [27]. This band disappears on complexation, suggesting chelation of the oxygen to the lead atom. The ν_{asym}(COO) and ν_{sym}(COO) stretching vibrations characteristic of the coordinated carboxylate anions were intense bands near 1,545 and 1,300 cm^{-1}, respectively [28]. The observed large separation between ν_{asym}(COO) and ν_{sym}(COO) stretching vibrations ($\Delta\nu = \nu_{asym}(COO) - \nu_{sym}(COO) \sim 245\ cm^{-1}$) for carboxylate group shows the bidentate nature of the ligands in the complexes. However, in the case of the free ligands and complexes, a strong band present at 1,720 $\pm$ 5 cm^{-1} in the free carboxylate region shows that in these complexes the carboxylate group is bonded to metal in a unidentate manner [29].

These results suggest that the azomethine nitrogen and carboxylate oxygen groups are involved in coordination with the lead(II) ion in the complexes. Several new bands appear in the complexes at $\sim$430 and $\sim$545 cm^{-1}, and are probably due to ν(Pb−O) [30] and ν(Pb←N) [30], respectively.

^{1}H NMR spectra

All the protons were found as to be in their expected regions [31]. The conclusions drawn from these studies lend further support to the mode of bonding discussed in

their IR spectra. In the spectra of lead(II) complexes, coordination of the ligands via azomethine nitrogen and carboxylate oxygen was established by the downfield shifting of these signals in the lead(II) complexes, because of the increased conjugation and coordination [32]. The number of protons calculated from the integration curves and those obtained from the values of the expected CHN analyses agree with each other. It was observed that DMSO had no coordinating effect either on the spectra of the ligands or on its metal complexes.

In the proton magnetic resonance spectra of the ligands, a sharp signal at $\sim\delta$ 1.80 ppm is observed, due to –C(CH_3)=N–. This moves downfield ($\sim\delta$ 0.10 ppm) in the complexes in comparison with its original position in the ligands, because of coordination of azomethine nitrogen to the metal atom. The ligands also give an OH proton signal at δ 11.20 $\pm$ 0.10 ppm (s) which is absent from the spectra of the corresponding lead complexes, showing thereby chelation of the ligand moiety through the deprotonated carboxylic oxygen. The ligands give a complex multiplet signal in the region δ 6.90–7.60 ppm (m) for the aromatic protons and this remains almost at the same position in the spectra of the metal complexes.

Schiff bases derived from glycine, alanine, valine, and isoleucine contain three aromatic protons, as expected. In the spectrum of phenylalanine, the integral of the aromatic region corresponds to eight protons; five protons on the phenyl ring are recognizable at ca. 7.2 ppm. With tryptophan, protons on the five-membered rings of the indole moieties give rise to signals partially overlapped with the aromatic proton signals. However, signals are still recognizable. Methyl (for glycine, methylene) protons on the α-carbon of the carboxylic acid moieties appear at 4.1–4.7 ppm. This signal is a singlet for (1), a quartet for (3), and doublet of doublets for (2) and (4), all of which arise from the non-equivalent methylene protons in structures (1), (5), and (6).

^{13}C NMR Spectra

^{13}C NMR spectra of the ligands and their corresponding lead complexes were recorded in dry DMSO. The signals for the carbon atoms attached to the carboxylate and azomethine groups in the ligands appear at $\sim\delta$ 177.2 ppm and $\sim\delta$ 162.1 ppm, respectively. However, in the spectra of the corresponding lead complexes, these appears at $\sim\delta$ 167.5 ppm (due to the carboxylate group) and $\sim\delta$ 156.4 ppm (due to the azomethine group), respectively. The considerable shifts in the positions of these signals clearly indicate the involvement of these functional groups in bond formation with the metal.

Although it is also possible that the shifting of the azomethine carbon signal is because of a change in hybridization of the nitrogen attached to the carboxylate group, in the light of IR, UV, and ^{1}H NMR spectral studies it seems more plausible that the shifting of the signals for these carbons because of the involvement of carboxylate oxygen and azomethine nitrogen in bonding.

^{19}F NMR Spectra

^{19}F NMR spectra of the ligands and the corresponding lead(II) complexes were recorded relative to hexafluorobenzene. Ligands give a single fluorine resonance peak at $\sim\delta$ −76.2 ppm whereas the lead(II) complexes show absorption peaks from δ −70.3 to δ −72.6 ppm. Similar downfield shifting in fluorine resonance chemical shift has been reported in the literature [33], and suggests non-involvement of the fluorine atom in bonding.

Therefore, four-coordinate square-planar geometry may be proposed for the resulting lead(II) complexes. Thus on the basis of the discussion above, it is clear that the ligand, by coordinating to the lead atom through the azomethine nitrogen, behaves as a bidentate ligand. Because all the resulting lead complexes are monomeric, the structure in Fig. 2 is proposed for the lead(II) complexes.

Conclusion

Complexes 1–6, derivatives of fluorinated Schiff bases, have been successfully synthesized and characterized. Elemental analysis C, H, N, and Pb results were in agreement with predicted formulae. Results from infrared and NMR spectroscopy of the ligands and complexes showed that coordination takes place via the oxygen atom from the carboxylate group and the nitrogen atom from the azomethine group. As a result, in the solid and liquid state the lead(II) complexes are in a four-coordinated environment around the metal atom.

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