



SYNTHESIS AND CHARACTERISATION OF SOME HEXAPHENYLENEDILEAD COMPOUNDS WITH MONOFUNCTIONAL BIDENTATE SCHIFF BASES

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ABSTRACT

Complexes of hexaphenyldilead with monofunctional bidentate Schiff bases in 1 : 2 molar ratio were synthesized and characterized by elemental analysis and spectral studies. All reactions were found to be quite facile and lead–lead bond was cleaved in preference to lead–carbon bond. The complexes of monofunctional bidentate Schiff bases were yellow solids. They are soluble in DMSO and DMF and quite stable in air and are not easily attacked by moisture. Molar conductance measurements show that these are non–electrolytic in nature. In these complexes, the central lead atom probably acquires coordination number of five and has trigonal bipyramidal structures.

Keywords : Hexaphenyldilead, Azomethines

INTRODUCTION

Lowing¹ reported the first synthesis of an organolead compound during the reaction of a sodium–lead alloy and ethyl iodide. Several organolead–nitrogen compounds have been the subjects of patents on account of their biological potency, particularly with respect to fungi. Kenny and Sowa *et al.*² claimed that lead derivatives of aminoethylene aldehydes are biocides whereas De Press³ had shown that compounds of the type triethyl (sec.–butylamine) lead are good herbicides. A number of Schiff base ligands have been reported for their bactericidal⁴, fungicidal⁵, antitumour⁶, anticancer⁷ and sterease inhibiting⁸ activities. As a consequence of their biological potency, there has been a growing interest in the study of lead (IV) complexes with nitrogen and oxygen donor ligands in recent years⁹. Keeping these facts in view, the reactions of hexaphenyldilead with monofunctional bidentate Schiff bases were carried out in 1 : 2 molar ratio. The reaction may be represented by the following general equation –



where, SBH = Monofunctional bidentate Schiff bases

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EXPERIMENTAL

Hexaphenyldilead decomposes thermally and was therefore protected from sunlight. Benzene and diethyl ether (Alembic) was stored over sodium wire for several days and then distilled after refluxing for a day. It was finally dehydrated by the azeotropic fractionation with ethanol. Chloroform (BDH) was stored over anhydrous calcium oxide and fractionated over aluminium isopropoxide. Hexaphenyldilead used was from Fisher, U.S.A.

The azomethines were prepared by condensing salicylaldehyde with an equimolecular amount of appropriate amines in benzene as a medium. Physical characteristics and analysis of these Schiff bases are summarized in Table 1.

Table 1. Reaction of hexaphenyldilead with N-[alkyl or aryl] salicylaldimine in molar ratio 1 : 2

| Schiff bases | Physical characteristics | | | Analysis (%) | | |
|---|--------------------------|---------|---------|------------------|-----------------|-----------------|
| | Colour and state | b.p. °C | m.p. °C | C found (Calc.) | H found (Calc.) | N found (Calc.) |
| N-[Ethyl]salicylaldimine HO.C ₆ H ₄ .CH:N.C ₂ H ₅ .(C ₉ H ₁₁ NO) | Dark yellow liquid | 74-75 | - | 72.57 (72.53) | 7.42 (7.44) | 9.35 (9.40) |
| N-[n-propyl]salicylaldimine HO.C ₆ H ₄ .CH:N-n-C ₃ H ₇ (C ₁₀ H ₁₃ NO) | Dark yellow liquid | 90-91 | - | 73.48 (73.53) | 7.87 (7.81) | 8.56 (8.65) |
| N-[iso-propyl]salicylaldimine HO.C ₆ H ₄ .CH:N-iso-C ₃ H ₇ (C ₁₀ H ₁₃ NO) | Dark yellow liquid | 52-55 | - | 73.68 (73.53) | 7.69 (7.81) | 8.70 (8.65) |
| N-[n-butyl]salicylaldimine HO.C ₆ H ₄ .CH:N-n-C ₄ H ₉ (C ₁₁ H ₁₅ NO) | Dark yellow liquid | 84-85 | - | 74.39 (74.49) | 8.36 (8.52) | 7.87 (7.93) |
| N-[iso-butyl]salicylaldimine HO.C ₆ H ₄ .CH:N-iso-C ₄ H ₉ (C ₁₁ H ₁₅ NO) | Dark yellow liquid | 102-105 | - | 74.31 (74.49) | 8.47 (8.52) | 7.85 (7.93) |
| N-[sec-butyl]salicylaldimine HO.C ₆ H ₄ .CH:N-sec-C ₄ H ₉ (C ₁₁ H ₁₅ NO) | Yellow liquid | 77 | - | 74.45 (74.49) | 8.53 (8.52) | 7.89 (7.93) |
| N-[tert.butyl]salicylaldimine HO.C ₆ H ₄ .CH:N-tert.C ₄ H ₉ | Yellow solid | | 95-96 | 74.44 (74.49) | 8.43 (8.52) | 7.90 (7.93) |
| N-[n-pentyl]salicylaldimine HO.C ₆ H ₄ .CH:N-nCH ₃ (CH ₂) ₄ (C ₁₂ H ₁₇ NO) | Yellow liquid | 80-85 | - | 75.28 (75.39) | 8.21 (8.39) | 7.17 (7.32) |
| N-[phenyl]salicylaldimine HO.C ₆ H ₄ .CH:N.C ₆ H ₅ (C ₁₃ H ₁₁ NO) | Yellow solid | 151 | 50 | 79.01 (79.12) | 5.63 (5.62) | 7.10 (7.12) |
| N-[α-methylphenyl]salicylaldimine HO.C ₆ H ₄ .CH:N- CH.C ₆ H ₅ (C ₁₄ H ₁₂ NO)Yellow solid | Yellow solid | - | 52-55 | 79.89 (79.97) | 5.79 (5.75) | 6.55 (6.66) |
| N-[o-tolyl]salicylaldimine HO.C ₆ H ₄ .CH:N- C ₆ H ₄ CH ₃ -m(C ₁₄ H ₁₃ NO) | Yellow solid | - | 44 | 79.86 (79.64) | 6.13 (6.20) | 6.61 (6.66) |

Continued...

Table 1. Continued.,...

| Schiff bases | Physical characteristics | | | Analysis (%) | | |
|---|--------------------------|---------------|--------|------------------|----------------|----------------|
| N-[m-tolyl]salicylaldimine HO.C ₆ H ₄ .CH:N.C ₆ H ₄ CH ₃ -m(C ₁₄ H ₁₃ NO) | Dark yellow liquid | 162-64 | - | 78.69 (79.64) | 6.03 (6.20) | 6.58 (6.66) |
| N-[o-methoxyphenyl]salicylaldimine HO.C ₆ H ₄ .CH:N.C ₆ H ₄ .OCH ₃ - o(C ₁₄ H ₁₃ NO ₂)Orange needle | Orange needle | - | 94 | 79.96 (79.64) | 6.07 (6.20) | 6.69 (6.66) |
| N-[o-methoxyphenyl]salicylaldimine HO.C ₆ H ₄ .CH:N.C ₆ H ₄ .OCH ₃ - o(C ₁₄ H ₁₃ NO ₂)Yellow solid | Yellow solid | - | 52 | 73.99 (74.01) | 5.69 (5.73) | 6.35 (6.17) |
| N-m-ethoxyphenyl]salicylaldimine HO.C ₆ H ₄ .CH:N.C ₆ H ₄ .OCH ₃ - m(C ₁₄ H ₁₃ NO ₂)Yellow solid | Yellow solid | 142- 3/0.1 | - | 74.07 (74.01) | 5.69 (5.73) | 6.07 (6.17) |
| N-[p-methoxyphenyl]salicylaldimine HO.C ₆ H ₄ .CH:N.C ₆ H ₄ OCH ₃ - p(C ₁₄ H ₁₃ NO ₂)Greyish green solid | Greyish green solid | - | 84 | 74.05 (74.01) | 5.70 (5.73) | 6.31 (6.17) |
| N-[p-chlorophenyl]salicylaldimine HO.C ₆ H ₄ .CH:N.C ₆ H ₄ Cl- p(C ₁₃ H ₁₀ Cl.NO)Yellow solid | Yellow solid | - | 88-90 | 67.32 (67.36) | 4.43 (4.35) | 6.11 (6.04) |
| N-[p-nitrophenyl]salicylaldimine HO.C ₆ H ₄ .CH:N.C ₆ H ₄ .NO ₂ - p(C ₁₃ H ₁₀ Cl.NO ₃) | Orange solid | - | 185-87 | 68.20 (68.39) | 4.47 (4.41) | 6.10 (6.13) |

Hexaphenyldilead (0.87 g.) was dissolved in benzene (25-30 mL) and N-[alkyl or aryl salicylaldimine (0.30-0.35 g) was slowly added. The contents were refluxed for about six hours. The light yellow solid compound was precipitated by petroleum ether (60-80°C) from the reaction mixture. The yellow precipitate was filtered and washed several times with petroleum ether. Table 2 records the physical properties of lead (IV) derivatives.

Table 2. Physical properties of lead (IV) derivatives of N-(alkyl or aryl) salicylaldimines

| S.No. | Compound | Colour/State | m.p. | Yield (%) |
|-------|--|---------------------|--------------|-----------|
| 1. | (C ₆ H ₅) ₃ Pb(C ₉ H ₁₀ NO) | Light yellow, solid | 237-239°C, d | 74 |
| 2. | (C ₆ H ₅) ₃ Pb(C ₁₀ H ₁₂ NO) | Yellow, solid | 231-233°C, d | 81 |
| 3. | (C ₆ H ₅) ₃ Pb(C ₁₀ H ₁₂ NO)* | Yellow, solid | 229-231°C, d | 78 |
| 4. | (C ₆ H ₅) ₃ Pb(C ₁₁ H ₁₄ NO) | Light yellow, solid | 230-231°C, d | 77 |
| 5. | (C ₆ H ₅) ₃ Pb(C ₁₁ H ₁₄ NO)* | Light yellow | 228-229°C, d | 70 |
| 6. | (C ₆ H ₅) ₃ Pb(C ₁₁ H ₁₄ NO)** | Light yellow, solid | 230-232°C, d | 77 |
| 7. | (C ₆ H ₅) ₃ Pb(C ₁₁ H ₁₄ NO) | Light yellow, solid | 230°C, d | 78 |

Continued...

Table 2. Continued,....

| S.No. | Compound | Colour/State | m.p. | Yield (%) |
|-------|---|---------------|--------------|-----------|
| 8. | (C ₆ H ₅) ₃ Pb(C ₁₂ H ₁₆ NO) | Yellow, solid | 272°C | 80 |
| 9. | (C ₆ H ₅) ₃ Pb(C ₁₃ H ₁₀ NO) | Yellow, solid | 228–229°C | 78 |
| 10. | (C ₆ H ₅) ₃ Pb(C ₁₄ H ₁₁ NO) | Yellow, solid | 225°C, d | 77 |
| 11. | (C ₆ H ₅) ₃ Pb(C ₁₄ H ₁₂ NO) | Yellow, solid | 226–227°C, d | 75 |
| 12. | (C ₆ H ₅) ₃ Pb(C ₁₄ H ₁₂ NO) | Yellow, solid | 238–240°C | 70 |
| 13. | (C ₆ H ₅) ₃ Pb(C ₁₄ H ₁₂ NO) | Yellow, solid | 238°C, d | 70 |
| 14. | (C ₆ H ₅) ₃ Pb(C ₁₄ H ₁₂ NO ₂) | Yellow, solid | 237°C, d | 82 |
| 15. | (C ₆ H ₅) ₃ Pb(C ₁₄ H ₁₂ NO ₂) | Yellow, solid | 235–236°C, d | 80 |
| 16. | (C ₆ H ₅) ₃ Pb(C ₁₄ H ₁₂ NO ₂) | Yellow, solid | 232–233°C, d | 67 |
| 17. | (C ₆ H ₅) ₃ Pb(C ₁₃ H ₉ ClNO) | Yellow, solid | 285–288°C | 78 |
| 18. | (C ₆ H ₅) ₃ Pb(C ₁₃ H ₉ N ₂ O ₃) | Yellow, solid | 229–231°C | 78 |

d = decomposed, * = iso, ** = sec.

RESULTS AND DISCUSSION

Triphenyllead (IV) complexes of monofunctional bidentate Schiff bases are yellow solids. These are soluble in DMSO and DMF, quite stable in air and are not easily attacked by moisture. Molar conductance measurements show that these are non-electrolytic in nature. In these complexes, the central lead atom probably acquires coordination number of five and has trigonal bipyramidal structures. The structure may be represented as follows –

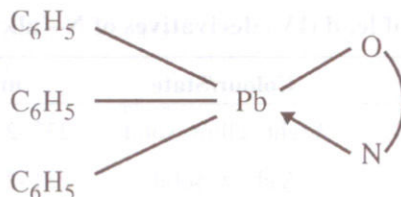


Table 3 records the important tentative assignments of infrared spectra of Schiff bases and their organo lead (IV) complexes on the basis of the data available in standards texts^{10,11}.

The infrared spectra of N-[alkyl or aryl] salicylaldimines show broad absorption bands of medium intensity in the region 3500–3300 cm⁻¹ and this may be attributed to CH or NH stretching modes. As the free –OH group absorbs at 3730–3520 cm⁻¹ and the free –NH group

in higher frequency side in lead (IV). Biradar *et al.*^{12,13} had the same observations in the lead (IV) complexes.

Table 3. Infrared frequencies of lead (IV) derivatives of N-(alkyl or aryl) salicylaldimines

| S.No. | $\gamma(\text{Pb-O})$ cm^{-1} | $\gamma(\text{Pb-N})$ cm^{-1} | $\gamma(\text{C=N})$ cm^{-1} | $\gamma(\text{C-O})$ stretching phenolic cm^{-1} | $\gamma(\text{C=C})$ cm^{-1} |
|-------|---|---|--|---|--|
| 1. | 475 (m) | 490 (s) | 1640 (s) | 1310 (s) | 1600 (m) |
| 2. | 455 (m) | 480 (s) | 1655 (s) | 1305 (s) | 1590 (m) |
| 3. | 475 (m) | 516 (s) | 1652 (s) | 1300 (s) | 1585 (s) |
| 4. | 457 (m) | 515 (s) | 1642 (s) | 1300 (s) | 1590 (m) |
| 5. | 470 (m) | 510 (s) | 1650 (s) | 1305 (s) | 1590 (m) |
| 6. | 460 (m) | 480 (s) | 1640 (s) | 1300 (s) | 1585 (s) |
| 7. | 455 (m) | 500 (s) | 1645 (s) | 1310 (s) | 1580 (m) |
| 8. | 460 (m) | 510 (s) | 1640 (s) | 1305 (s) | 1495 (s) |
| 9. | 465 (m) | 525 (s) | 1645 (s) | 1305 (s) | 1495 (m) |
| 10. | 460 (m) | 525 (s) | 1640 (s) | 1310 (s) | 1600 (m) |
| 11. | 460 (m) | 500 (m) | 1640 (s) | 1310 (m) | 1580 (s) |
| 12. | 470 (m) | 505 (s) | 1645 (s) | 1305 (m) | 1600 (s) |
| 13. | 480 (m) | 515 (s) | 1642 (s) | 1300 (m) | 1580 (sp) |
| 14. | 470 (m) | 505 (s) | 1645 (s) | 1310 (s) | 1590 (s) |
| 15. | 465 (m) | 490 (s) | 1640 (s) | 1315 (s) | 1595 (s) |
| 16. | 465 (m) | 500 (s) | 1650 (s) | 1310 (s) | 1585 (m) |
| 17. | 475 (s) | 515 (s) | 1650 (s) | 1315 (s) | 1590 (sp) |
| 18. | 465 (m) | 510 (s) | 1645 (s) | 1310 (s) | 1590 (sp) |

s = strong, m = medium, sp = sharp.

The metal–ligand, metal–oxygen and metal–nitrogen vibration modes are generally found to occur in the region of $600\text{--}400\text{ cm}^{-1}$. Several new bands in the region $600\text{--}400\text{ cm}^{-1}$ may be attributed to $\nu(\text{Pb-N})$ and $\nu(\text{Pb-O})$ vibrations. However, it is not easy to assign $\nu(\text{Pb-N})$ and $\nu(\text{Pb-O})$ vibration in these complexes because various skeletal vibrations of the ligands interfere with $\nu(\text{Pb-N})$ and $\nu(\text{Pb-O})$ vibrations. These complexes are probably five coordinated and have trigonal bipyramidal structure with a planar triorgano lead moiety, which is common in the elements of this group.

Electronic spectra of the complexes

The electronic spectra of N-[alkyl or aryl] salicylaldimine Schiff bases and their corresponding triphenyl lead (IV) derivatives have been recorded in DMF at room temperature. The spectra of the ligand and their corresponding complexes were found to lead to the following conclusions.

Electronic spectra of N-[alkyl or aryl] salicylaldimines show a maxima in the region 375–390 nm, which may be assigned to the $n \rightarrow \pi^*$ transition of the azomethine group ($>C=N-$) and in the spectra of their corresponding triphenyl lead (IV) derivatives. This band has shifted to the lower wavelength. It suggests the donation of the lone pair of electrons by the nitrogen atom of the azomethine group to the central lead atom and thereby making their transition to the higher energy level rather difficult.

A band appeared in the region 310–315 nm in all the spectra, which may be assigned to $\pi \rightarrow \pi^*$ electronic transitions of the azomethine grouping. A band appeared at 250–255 nm in the spectra of N-[alkyl or aryl] salicylaldimenes and their triphenyl lead (IV) complexes, which may be assigned to electronic transitions of the benzenoid ring.

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Accepted : 27.1.2005