

Synthesis and Characterization of Some Hexaphenyldilead Complexes with Bifunctional Tridentate Schiff Bases

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The reactions of hexaphenyldilead with bifunctional tridentate Schiff bases in 1:2 molar ratios have been studied in anhydrous benzene. All the reactions were found to be quite facile and lead-lead bond was cleaved in preference to the lead-carbon bond. The resulting derivatives were yellow solids. They are quite stable in air and are not easily attacked by moisture. They are soluble in DMF and DMSO only. The lead atom, in these complexes, has a coordination number of six.

Key Words: Synthesis, Hexaphenyldilead, Complexes, Tridentate Schiff bases.

INTRODUCTION

Continuing with our endeavour¹ of cleaving lead-lead bond in hexaphenyldilead (IV) with monofunctional bidentate Schiff bases, we extend the present investigation with bifunctional tridentate Schiff bases as potential ligands. The lead-lead bond cleaves within 8-10 h. The reaction of hexaphenyldilead (IV) with bifunctional tridentate Schiff bases in 1:2 molar ratios can be represented by the following general equation:



(where SBH_2 = Bifunctional tridentate Schiff bases).

EXPERIMENTAL

Hexaphenyldilead decomposes thermally and also in light. It was therefore, protected from heat and sunlight. Chloroform (BDH) was stored over anhydrous calcium oxide. Diethyl ether (Alembic) was stored over sodium wire for 2 h, refluxed and then distilled at 35 °C. All glass apparatus fitted with quick-fit interchangeable standard ground joints were washed and dried in oven at 120-130 °C.

Preparation of bifunctional tridentate Schiff bases: The following Schiff bases were prepared by the condensation of salicylaldehyde, *o*-hydroxyacetophenone, 2,4-pentanedione and 2-hydroxy-1-naphthaldehyde with alcoholic amines in equimolecular ratio in benzene medium.

The contents were refluxed for 5-6 h on a fractionating column and after removing the solvent, they were purified by distillation under reduced pressure.

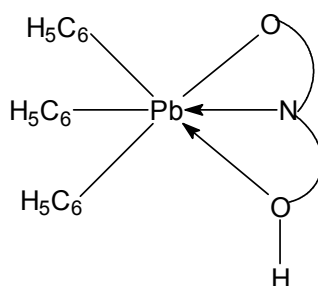
The resulting Schiff bases are: N-(2-hydroxyethyl)salicylaldimine; N-(2-hydroxy-1-propyl)salicylaldimine; N-(3-hydroxy-1-propyl)salicylaldimine; N-(2-hydroxyethyl) *o*-hydroxyacetophenoneimine; N-(2-hydroxy-1-propyl) *o*-hydroxyacetophenoneimine; N-(3-hydroxy-1-propyl) *o*-hydroxyacetophenoneimine; 4-(2-hydroxyethyl)amino-3-pentene-2-one; 4-(2-hydroxy-1-propyl)amino-3-pentene-2-one; 4-(3-hydroxy-1-propyl)amino-3-pentene-2-one; N-(2-hydroxyethyl)-2-hydroxy-1-naphthaldimine.

Schiff bases belonging to this group possess two functional (–OH) groups and one OH besides the characteristics azomethine (–C=N–) group and thus have three possible sites of coordination. These Schiff bases have ONO donor system and their corresponding anions as –SBH₂ or –SB–, obtained by the liberation of one or two protons, respectively. The physical characteristics and analysis of these Schiff bases have been recorded in Table-1.

Reactions of hexaphenyldilead with Schiff bases: Hexaphenyldilead (0.87 g) was dissolved in benzene (30 mL) and bifunctional tridentate Schiff bases (0.33-0.40 g as required) was added. The reaction mixture was refluxed for about 8 h. Excess of benzene was pumped out under reduced pressure. On adding petroleum ether at (60-80 °C) and keeping it in ice, yellow crystals were obtained.

RESULTS AND DISCUSSION

The resulting complexes are yellow solids. They are soluble in DMF and DMSO and have limited solubility in common organic solvents. The physical properties of these complexes have been presented in Table-2. In these complexes, lead atom attains a coordination of six.



Infrared spectra of Schiff bases and corresponding organolead (IV) complexes have been scanned and important tentative assignments have been made on the basis of the data available in the standard literature². These assignments have been recorded in Table-3. A strong band in the

TABLE-1
CHARACTERISTICS AND ANALYSIS OF BIFUNCTIONAL TRIDENTATE SCHIFF BASES

Schiff bases	Colour	b.p. / (m.p.)	Elemental analysis: Found (Calcd.) (%)		
			C	H	N
N-(2-hydroxyethyl) salicylaldimine	Yellow viscous liquid	138	65.30 (65.45)	6.50 (6.66)	8.45 (8.48)
HO-C ₆ H ₄ -CH:N-CH ₂ CH ₂ OH (C ₉ H ₁₁ NO ₂)					
N-(2-hydroxy-1-propyl) salicylaldimine	Yellow liquid	127	67.00 (67.04)	7.29 (7.26)	7.65 (7.82)
HO-C ₆ H ₄ -CH:N-CH ₂ -CHOH-CH ₃ (C ₁₀ H ₁₃ NO ₂)					
N-(3-hydroxy-1-propyl) salicylaldimine	Yellow liquid	152	67.10 (67.04)	7.41 (7.26)	7.61 (7.82)
HO-C ₆ H ₄ -CH:N-CH ₂ CH ₂ CH ₂ -OH (C ₁₀ H ₁₃ NO ₂)					
N-(2-hydroxyethyl) o-hydroxy acetophenoneimine	Dark yellow solid	(95)	67.81 (67.04)	7.32 (7.26)	7.98 (7.82)
HO-C ₆ H ₄ -C-CH ₃ :N-CH ₂ :CH ₂ -OH (C ₁₀ H ₁₃ NO ₂)					
N-(2-hydroxy-1-propyl) o-hydroxy acetophenoneimine	Yellow solid	(91)	68.39 (68.39)	7.81 (7.77)	7.27 (7.25)
HO-C ₆ H ₄ -C-CH ₃ :N-CH ₂ :CHOH-CH ₃ (C ₁₁ H ₁₅ NO ₂)					
N-(3-hydroxy-1-propyl) o-hydroxy acetophenoneimine	Yellow solid	(77)	68.37 (68.39)	7.86 (7.77)	7.25 (7.25)
HO-C ₆ H ₄ -C-CH ₃ :N-CH ₂ :CH ₂ CH ₂ OH(C ₁₁ H ₁₅ NO ₂)					
4-(2-hydroxyethyl)amino-3-pentene-2-one	Dark yellow needles	(73)	58.85 (58.74)	9.18 (9.09)	9.70 (9.79)
CH ₃ :CO-CH-C-CH ₃ :NH-CH ₂ :CH ₂ :OH(C ₇ H ₁₃ NO ₂)					
4-(2-hydroxy-1-propyl)amino-3-pentene-2-one	Pale yellow	(82)	61.30 (61.14)	9.65 (9.55)	8.86 (8.92)
CH ₃ CO-CHCCH ₃ :NHCH ₂ :CH-OH-CH ₃ (C ₈ H ₁₅ NO ₂)					
4-(3-hydroxy-1-propyl)amino-3-pentene-2-one	Yellow liquid	117	61.00 (61.14)	9.67 (9.55)	9.11 (8.92)
CH ₃ CO-CHC-CH ₃ :NH-CH ₂ :CH ₂ :OH(C ₈ H ₁₅ NO ₂)					
N-(2-hydroxyethyl) 2-hydroxy-1-naphthaldimine	Light greenish yellow solid	(152-155)	72.59 (72.56)	6.00 (6.05)	6.53 (6.51)
HO-C ₁₀ H ₆ -CH:N-(CH ₂) ₂ -OH (C ₁₃ H ₁₃ NO ₂)					

TABLE-2
 PHYSICAL PROPERTIES OF LEAD (IV) DERIVATIVE OF
 N-(HYDROXYL ALKYL) ALDIMINES

Code	Complex/ (colour)	m.p. (°C) / Yield (%)	Elemental analysis: Found (Calcd.) %			
			C	H	N	Pb
C ₁	(C ₆ H ₅) ₃ Pb(C ₉ H ₁₀ NO ₂) (Light yellow solid)	240 (87)	53.76 (53.82)	4.22 (4.15)	2.23 (2.32)	34.07 (34.38)
C ₂	(C ₆ H ₅) ₃ Pb(C ₁₀ H ₁₂ NO ₂) (Light yellow solid)	238† (85)	54.45 (54.54)	4.43 (4.38)	2.20 (2.27)	33.18 (33.60)
C ₃	(C ₆ H ₅) ₃ Pb(C ₁₀ H ₁₂ NO ₂) (Yellow solid)	236-237† (72)	54.37 (54.54)	4.45 (4.38)	2.24 (2.27)	32.89 (33.60)
C ₄	(C ₆ H ₅) ₃ Pb(C ₁₃ H ₁₂ NO ₂) (Yellow solid)	207-209 (78)	56.89 (57.05)	4.13 (4.14)	2.02 (2.14)	30.67 (31.74)
C ₅	(C ₆ H ₅) ₃ Pb(C ₁₀ H ₁₂ NO ₂) (Yellow solid)	236† (91)	54.57 (54.54)	4.40 (4.38)	2.20 (2.27)	32.67 (33.60)
C ₆	(C ₆ H ₅) ₃ Pb(C ₁₀ H ₁₂ NO ₂) (Yellow solid)	239† (82)	55.10 (54.54)	4.59 (4.38)	2.18 (2.27)	32.76 (33.60)
C ₇	(C ₆ H ₅) ₃ Pb(C ₁₁ H ₁₄ NO ₂) (Light yellow solid)	238† (83)	55.17 (55.23)	4.58 (4.60)	2.16 (2.22)	31.27 (32.86)
C ₈	(C ₆ H ₅) ₃ Pb(C ₇ H ₁₂ NO ₂) (Light yellow solid)	195-297† (81)	51.59 (52.63)	4.65 (4.73)	2.37 (2.45)	34.78 (36.31)
C ₉	(C ₆ H ₅) ₃ Pb(C ₈ H ₁₄ NO ₂) (Light yellow solid)	185-287† (87)	52.39 (52.52)	4.87 (4.88)	2.30 (2.35)	33.71 (34.85)
C ₁₀	(C ₆ H ₅) ₃ Pb(C ₈ H ₁₄ NO ₂) (Yellow solid)	183-185† (78)	52.93 (52.52)	4.87 (4.88)	2.31 (2.35)	34.01 (34.85)

† = Decomposed.

region 1280-1275 cm⁻¹ due to phenolic (C–O) stretching vibration disappeared in these complexes, which suggests that phenolic oxygen is covalently bonded with lead atom³ in complexation.

A broad band due to intermolecularly bonded –OH group appears in the region 3500-3300 cm⁻¹ in the spectra of Schiff bases shifts towards the high frequency side and is observed in the region 3755 ± 5 cm⁻¹ (C₁-C₄ complexes). Shifting to the higher frequency can be explained by the absence of hydrogen bonding due to the coordination of alcoholic oxygen to the central lead atom, thus giving rise to a stable octahedral structure to these complexes.

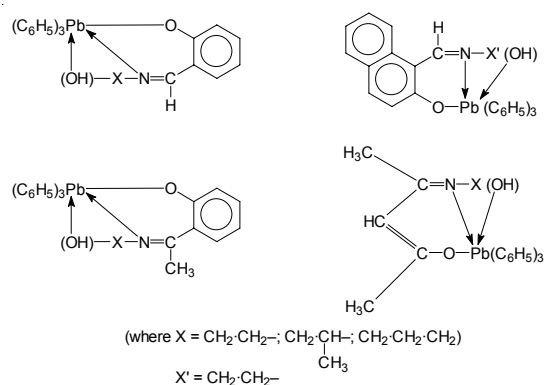
A strong band appeared in the region 1630-1600 cm⁻¹ in the IR spectra of Schiff bases assignable to the azomethine (>C=N–) group shifts to higher frequency region 1640-1635 cm⁻¹ in all complexes except in C₈-C₁₀ in which it is present at 1600-1590 cm⁻¹. It suggests coordination through the azomethine nitrogen to lead atom in the complexes.

TABLE-3
 INFRARED FREQUENCIES (cm^{-1}) OF LEAD (IV) DERIVATIVES OF
 N-(HYDROXYALKYL) ALDIMINES

Complex code	$\nu(\text{Pb-O})$	$\nu(\text{Pb-N})$	$\nu(\text{C=N})$	$\nu(\text{C=C})$	$\nu(\text{OH})$
C ₁	470 m	505 s	1645 s	1595 m	3755 b
C ₂	485 m	515 s	1642 vs	1590 m	3750 b
C ₃	475 m	515 s	1641 vs	1592 m	3750 b
C ₄	470 m	525 s	1635 s	1595 m	3750 b
C ₅	470 m	520 s	1640 vs	1595 m	3750 b
C ₆	460 m	525 s	1641 vs	1590 m	3750 b
C ₇	470 m	530 s	1635 vs	1590 m	3755 b
C ₈	475 m	525 s	1600 s	1575 m	3750 b
C ₉	480 m	500 s	1590 s	1570 m	3755 b
C ₁₀	485 m	520 s	1695 vs	1575 m	3755 b

Metal-ligand, metal-oxygen and metal-nitrogen vibrations are generally found to occur between $600\text{-}200\text{ cm}^{-1}$ regions. However, in these complexes, it is not easy to assign $\nu(\text{Pb-O})$ and $\nu(\text{Pb-N})$ vibrations because various skeletal variations of the Schiff bases interfere with them.

Infrared spectra of these complexes (from C₁-C₄) show a strong band in the region $575\text{-}515\text{ cm}^{-1}$ in C₁-C₄, $530\text{-}520\text{ cm}^{-1}$ in C₅-C₇ and $525\text{-}500\text{ cm}^{-1}$ in C₈-C₁₀ complexes may be attributed to $\nu(\text{Pb-N})$ vibration. Two new bands of medium intensity appear in $490\text{-}460\text{ cm}^{-1}$ region C₁-C₄, $470\text{-}460\text{ cm}^{-1}$ in C₅-C₇ and $485\text{-}475\text{ cm}^{-1}$ in C₈-C₁₀ complexes. In these complexes the central lead atom appears to be hexacoordinated. The structures may be octahedral and can be represented as below:



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(Received: 11 November 2006; Accepted: 14 September 2007) AJC-5841