COMPLEXES OF ZINC(II)

Coates and his coworkers (29) have prepared the complexes of zinc(II) iodide with p-dimethylaminophenyl dimethyl phosphine and p-dimethylaminophenyl diethyl phosphine and compared them with those formed by unsubstituted ligands. The introduction of a p-dimethylamino group in the ligand increases the stability of the complexes. Curran and coworkers (162) have prepared the complex ZnCl$_2$.2Et$_3$P by distilling triethyl phosphine under nitrogen atmosphere into an aqueous solution of zinc chloride. Yoke and Hatfield (94) have prepared and studied the complexes of zinc(II) halides with triethyl phosphine. All the complexes have the general composition ZnX$_2$.2(Et$_3$P) and have negligible dissociation pressures. Coates and Ridley (59a) have prepared and studied the low frequency infrared spectra of the complexes of zinc(II) chloride and zinc(II) bromide with triethylphosphine, phenyldimethylphosphine, p-dimethylaminophenyl dimethyl phosphine and triphenyl phosphine.

Noltes and Hark (145) have reported the preparation of the complexes of dibutyl-, diphenyl- and bis(pentafluorophenyl)zinc with triphenyl phosphine and have studied the influence of organic groups attached to zinc on the stability of these complexes.

Yoke and Hatfield (94) have employed diethylphosphine and ethyl phosphine for complex formation with zinc(II) chloride.
Wymore and Bailar (191) have reacted the ditertiary phosphine 1,2-bis(diethylphosphine)ethane with zinc(II) bromide to get the complex $[\text{Zn(diphos)}\text{Br}]_2$. Coates and Ridley (59a) have studied the preparation and low frequency infrared spectra of the complexes of zinc(II) chloride and zinc(II) bromide with the bidentate phosphine 1,2-bis(diphenylphosphino)ethane. Seidel (165) has obtained the complex $\text{Zn(diphos)}\text{I}_2$ by reacting dipiperidinodicyclohexyl diphosphine with zinc(II) iodide. Seidel (166) has also prepared a similar complex of zinc(II) iodide with dipiperidinodiphenyl diphosphine. This complex has been found to have relatively lower stability and readily decomposes into the monophosphine complex.

In the present investigation, the complexes of zinc(II) chloride, bromide and iodide with the ditertiary phosphines 1,2-bis(diphenylphosphino)ethane (DFE) and 1,4-bis(diphenylphosphino)butane (DPB) have been prepared and studied.

The zinc(II) halides (chloride, bromide and iodide) react with both the diphosphines 1,2-bis(diphenylphosphino)ethane and 1,4-bis(diphenylphosphino)butane when their solutions in ethanol in the molar ratio of 1.5:1 are mixed together followed by vigorous shaking. The complexes have been assigned the general formula $[\text{Zn(diphos)}X_2]$ on the basis of elemental analysis and are listed in Table IV-1.
<table>
<thead>
<tr>
<th>S. No.</th>
<th>Name of the complex</th>
<th>Colour</th>
<th>Melting point °C</th>
<th>Molar conductance in nitrobenzene ohm⁻¹cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Dichloro 1,2-bis(diphenylphosphino)ethane-zinc(II)</td>
<td>White</td>
<td>290</td>
<td>1.31</td>
</tr>
<tr>
<td>2.</td>
<td>Dibromo 1,2-bis(diphenylphosphino)ethane-zinc(II)</td>
<td>White</td>
<td>284-85</td>
<td>1.02</td>
</tr>
<tr>
<td>3.</td>
<td>Di-iodo 1,2-bis(diphenylphosphino)ethane-zinc(II)</td>
<td>White</td>
<td>Above 290</td>
<td>1.30</td>
</tr>
<tr>
<td>4.</td>
<td>Dichloro 1,4-bis(diphenylphosphino)butane-zinc(II)</td>
<td>White</td>
<td>250-52</td>
<td>1.71</td>
</tr>
<tr>
<td>5.</td>
<td>Dibromo 1,4-bis(diphenylphosphino)butane-zinc(II)</td>
<td>White</td>
<td>240-43</td>
<td>1.02</td>
</tr>
<tr>
<td>6.</td>
<td>Di-iodo 1,4-bis(diphenylphosphino)butane-zinc(II)</td>
<td>White</td>
<td>240-41</td>
<td>1.62</td>
</tr>
</tbody>
</table>
All the complexes are white crystalline solids and are fairly stable towards atmospheric moisture.

The complexes are thermally quite stable as indicated by their fairly high melting points (Table IV-1). The complexes formed by 1,2-bis(diphenylphosphino)ethane have higher melting points than those of the corresponding complexes given by 1,4-bis(diphenylphosphino)butane. This is in keeping with the similar trend observed in case of the complexes of d^{10} metal ions mercury(II) and cadmium(II). An attempt to study the mode of decomposition of the complexes with rise in temperature on the thermobalance proved unsuccessful because they swell and flow out of the crucible with rise in temperature.

The molar conductance of the complexes has been determined with millimolar solutions in nitrobenzene. The values of molar conductance of these complexes are given in Table IV-1. All the complexes have very low conductivity and obviously exist almost entirely as non-electrolytes. The little conductance is probably due to small amount of change-over to either \([\text{Zn(diphos)X.PhNO}_2]^{+}X'\) or more probably to \([\text{Zn(diphos)}_2]^{2+}[\text{ZnX}_4]^{2-}\). A similar observation has been made by Nyholm and his coworkers (128) in case of the zinc(II) halide complexes with the ditertiary arsine o-phenylene bis(dimethylarsine). An analogous complex of zinc(II) bromide with the ditertiary phosphine, 1,2-bis
(diethylphosphino)ethane has also been found to be non-conducting by Wymore and Bailar (191).

An unsuccessful attempt has been made to determine the molecular weights of the complexes in nitrobenzene by cryoscopic method but their low solubility was the main handicap. Rast's method for the determination of their molecular weights also failed as there was no depression in the melting point indicating their insolubility in molten camphor.

Zinc(II) is a d¹⁰ metal ion which, in its complexes, has usually coordination number four though sometimes six is also encountered. There are no ligand field stabilization effects in the zinc(II) ion because of d¹⁰ configuration. Consequently the factors determining the stereochemistry of its complexes are their size, electrostatic and covalent bonding forces. By analogy with the complexes formed by zinc(II) and Cd(II) halides formed with monotertiary phosphines (79), ditertiary phosphines (191) and ditertiary arsine (128), the complexes under discussion are believed to have got a four coordinate tetrahedral stereochemistry around zinc atom and they have the chelate structure:

\[
\begin{align*}
\text{C}_{\text{H}_3} & \quad \text{X} \\
\text{C}_{\text{H}_5} & \quad \text{C}_{\text{H}_3} \\
\text{X} & \quad \text{X}
\end{align*}
\]

\( n = 2 \) and \( 4 \)

\( X = \text{Cl}, \text{Br} \) and \( \text{I} \).
Experimental

Dichloro 1,2-bis(diphenylphosphino)ethane-zinc(II)

The ligand DPE (1.0 g.) was dissolved in ethanol (50 ml.) by refluxing on a water bath and zinc(II) chloride (1.0 g.) was dissolved in ethanol (25 ml.) in the cold. The two solutions were mixed with vigorous shaking when white complex separated out. It was filtered, washed with alcohol and dried under vacuum.

Found: Cl, 13.04, 12.92; Zn, 11.72, 11.65; P, 11.65, 11.82.
C\textsubscript{26}H\textsubscript{24}P\textsubscript{2}Cl\textsubscript{2}Zn requires Cl, 13.29; Zn, 12.22; P, 11.41.
Molar conductance in nitrobenzene is 1.31 ohm\textsuperscript{-1}cm\textsuperscript{1}.

Dibromo 1,2-bis(diphenylphosphino)ethane-zinc(II)

The ligand DPE (1.0 g.) was dissolved in ethanol (50 ml.) by refluxing on a water bath and zinc(II) bromide (0.8 g.) was dissolved in alcohol (30 ml.) separately. The two solutions were mixed with vigorous shaking when a white complex separated out almost immediately. It was filtered, washed with alcohol and dried under vacuum.

Found: Br, 25.40, 25.26; Zn, 10.20, 9.96; P, 10.00, 10.17.
C\textsubscript{26}H\textsubscript{24}P\textsubscript{2}Br\textsubscript{2}Zn requires Br, 25.67; Zn, 10.48 and P, 9.93.
Molar conductance in nitrobenzene is 1.02 ohm\textsuperscript{-1}cm\textsuperscript{1}.
Di-iodo 1,2-bis(diphenylphosphino)ethane-zinc(II)

The ligand DPS (0.8 g.) was dissolved in alcohol (50 ml.) by refluxing on a water bath whereas zinc(II) iodide (0.65 g.) was dissolved in alcohol (20 ml.) separately. On mixing the two solutions and vigorous shaking the white complex separated out. It was filtered, washed with alcohol and dried under vacuum.

Found: I, 34.87, 34.80; Zn, 8.91, 8.71; P, 8.34, 8.22.

\( C_{26}H_{24}P_2I_2Zn \) requires I, 35.37; Zn, 9.10, P, 8.63.

Molar conductance in nitrobenzene is 1.3 ohm\(^{-1}\)cm\(^{-1}\).

Dichloro 1,4-bis(diphenylphosphino)butane-zinc(II)

The ligand DPB (0.8 g.) was dissolved in alcohol (60 ml.) by refluxing on a water bath and zinc(II) chloride (0.5 g.) was dissolved in alcohol (20 ml.) separately. The solutions were mixed and on shaking a white complex separated out. It was filtered, washed with alcohol and dried under vacuum.

Found: Cl, 12.10, 11.98; Zn, 11.01, 10.95; P, 10.86, 10.68.

\( C_{28}H_{28}P_2Cl_2Zn \) requires Cl, 12.62; Zn, 11.56; P, 11.01.

Molar conductance in nitrobenzene is 1.71 ohm\(^{-1}\)cm\(^{-1}\).

Dibromo 1,4-bis(diphenylphosphino)butane-zinc(II)

A solution of DPB (0.8 g.) in alcohol (60 ml.), prepared by refluxing, was added to a solution of zinc(II) bromide (0.8 g.) in alcohol (25 ml.). The mixture was vigorously shaken
when the white complex separated out. It was filtered, washed with alcohol and dried under vacuum.


C_{28}H_{28}P_{2}Br_{2}Zn requires Br, 24.57; Zn, 9.98; P, 9.50.

Molar conductance in nitrobenzene is 1.02 ohm\(^{-1}\)cm\(^{-1}\).

Di-iodo 1,4-bis(diphenylphosphino)butane-zinc(II)

The ligand DPB (0.8 g.) was dissolved in ethanol (50 ml.) by refluxing on a water bath and zinc(II) iodide (0.8 g.) was dissolved in ethanol (50 ml.) separately in the cold. The two solutions were mixed with thorough shaking when the white complex separated out almost immediately. It was filtered, washed with ethanol and dried under vacuum.

Found: I, 33.45, 33.40; Zn, 8.18, 8.12; P, 7.92, 7.83.

C_{28}H_{28}P_{2}I_{2}Zn requires I, 34.09; Zn, 8.72; P, 8.30.

Molar conductance in nitrobenzene is 1.62 ohm\(^{-1}\)cm\(^{-1}\).

***************