COMPLEXES OF CADMIUM(II)

Purdie and his coworkers (79) have prepared complexes of cadmium(II) halides with a number of mono tertiary phosphines. They have isolated three distinct classes of non-ionic complexes with the general formulae \([R_3P]_2CdX_2\), \([R_3P]_2(CdX_2)_2\) and \([R_3P]_3(CdX_2)_2\) and have discussed their structures. Coates and coworkers (28,29) have studied the cadmium (II) halide complexes with phenyldimethylphosphine, p-dimethylaminophenyldimethyl phosphine, phenyldiethyl phosphine, p-dimethylaminophenyldiethyl phosphine and p-trifluoromethylphenyldiethyl phosphine. The substitution of a p-dimethylamino group increases the stability of the complexes, while p-trifluoromethyl group has the opposite effect. Deacon (70) has reported the preparation of complexes of cadmium(II) halides (bromide and iodide) with triphenyl phosphine and studied their reaction with alkyl halides. Coates and Ridley (59a) have prepared and studied the metal-halogen stretching frequencies of the complexes of cadmium(II) chloride with a number of ligands including phenyldimethyl phosphine and p-dimethylaminophenyldimethyl phosphine. On the basis of these low frequency infrared spectra, the complexes have been assumed to have chlorine bridged dimeric structure. Seidel (165) has reported the preparation of the complex \([C_6H_{10}N]_2(C_6H_{11})P.CdI_2\).
The complexes of cadmium(II) halides with primary and secondary phosphines do not appear to have been reported in literature.

Wymore and Bailar (191) have used the bidentate ligand 1,2-bis(diethylphosphino)ethane to get the complex Cd(diphos)Br₂. Seidel (166,167) has employed the ligands piperidinotricyclohexyl diphosphine, dipiperidinodicyclohexyl diphosphine and dipiperidinodiphenyl diphosphine to prepare complexes with cadmium(II) halides. The complexes with dipiperidinodiphenyl diphosphine have been found to have lower stability than those with dipiperidinodicyclohexyl diphosphine and they readily decompose into monophosphine complexes and cyclopolyphosphines. Coates and Ridley (59a) have prepared and studied the low frequency infrared spectra of the complexes of cadmium(II)chloride and bromide with the ditertiary phosphine 1,2-bis(diphenylphosphino)ethane.

In the present study, the complexes of cadmium(II) halides (chloride, bromide and iodide) with the ditertiary phosphines 1,2-bis(diphenylphosphino)ethane (DPE) and 1,4-bis(diphenylphosphino)butane (DPB) have been prepared with a view to make a comparative study of their properties.

Both the ligands DPE and DPB react with the halides (chloride, bromide and iodide) of cadmium(II) in ethanol to yield 1:1 complexes which have been assigned the general formula [Cd(diphos)X₂] on the basis of their elemental analysis.
All the complexes are crystalline white solids which separated out almost immediately. All of them are fairly stable towards atmospheric moisture. These are recorded in Table V-1.

Molar conductance of the complexes has been determined by preparing millimolar solutions of the complexes in nitrobenzene. The values of molar conductance of these complexes are given in Table V-1. All the complexes have very low conductivity and obviously exist almost entirely as non-electrolytes. The little conductivity may be due to small amount of changeover to either \([\text{Cd(diphos)X}_2\text{PhNO}_2]^+X^-\) or more probably to \([\text{Cd(diphos)}_2]^{2+}[(\text{CdX}_4)]^{2-}\). This is in accordance with the non-ionic behaviour of the complexes of cadmium(II) halides with monotertiary phosphines and arsines (79) and with the ditertiary arsine o-phenylenebis(dimethylarsine) (128).

Wymore and Bailar (191) have also reported that the complex \(\text{Cd(diphos)Br}_2\) (where diphos is 1,2-bis(diethylphosphino)ethane) is non-conducting in nitrobenzene. These workers have also isolated the complex \(\text{Cd}_2(\text{diphos})\text{Br}_6\).

The complexes are thermally quite stable as indicated by their fairly high melting points (Table V-1). A comparison of the melting points of the corresponding complexes with the two diphosphines shows that DPE complexes have relatively higher melting points than those of DPB complexes. An unsuccessful attempt has been made to determine the molecular weights of the complexes in nitrobenzene by cryoscopic method but their low
<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 (Ω⁻¹ cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dibromo 1,4-bis(diphenylphosphino)butane-cadmium (II)</td>
<td>White</td>
<td>265-66</td>
<td>1.14</td>
</tr>
<tr>
<td>2</td>
<td>Diiodo 1,4-bis(diphenylphosphino)butane-cadmium (II)</td>
<td>White</td>
<td>285</td>
<td>1.00</td>
</tr>
<tr>
<td>3</td>
<td>Dichloro 1,2-bis(diphenylphosphino)ethane-cadmium (II)</td>
<td>White</td>
<td>280-85</td>
<td>1.07</td>
</tr>
<tr>
<td>4</td>
<td>Dibromo 1,2-bis(diphenylphosphino)ethane-cadmium (II)</td>
<td>White</td>
<td>260-62</td>
<td>1.02</td>
</tr>
<tr>
<td>5</td>
<td>Diiodo 1,2-bis(diphenylphosphino)ethane-cadmium (II)</td>
<td>White</td>
<td>255</td>
<td>0.77</td>
</tr>
<tr>
<td>6</td>
<td>Dichloro 1,2-bis(diphenylphosphino)ethane-cadmium (II)</td>
<td>White</td>
<td>242-43</td>
<td></td>
</tr>
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solubility is the main handicap. East's method for the determination of molecular weights also failed as there was no depression in the melting point indicating their insolubility in molten camphor.

All the complexes have been subjected to thermogravimetric analysis. The mode of decomposition of all these complexes with rise in temperature is depicted by thermogramms (Figs. V-1 and V-2). It has not been possible to study the nature of intermediates or even the decomposition product. The small rise in the weight in the initial stages in case of some complexes may be due to the partial oxidation of the complexes to the diphosphine oxide complexes, but the exact rise in weight does not correspond to the theoretical value required for complete oxidation of the complex concerned.

Cadmium(II) is a d^{10} metal ion which, in its complexes, has coordination number six but more often four. Like zinc(II), the cadmium(II) ion also has its d orbitals completely occupied by electrons as a result of which there are no ligand field stabilisation effects in it. Consequently the factors determining the stereochemistry of cadmium(II) complexes are their size, electrostatic and covalent bonding forces. In the solid state, cadmium(II) halides appear to have six coordination number. However, Mann and his coworkers (79) who have prepared three types of complexes of monotertiary phosphines and arsines with cadmium(II) halides, have assigned
FIG. V-1

T.G.A. CURVES
- DPE Cd Cl₂
- DPE Cd Br₂
- DPE Cd I₂
tetrahedral configuration to these complexes. The complexes of the type \([R_3P_2(CdX_2)_2]\) which can theoretically exist in any one of the three bridged structures I, II or III, were assigned structure III because crystallographic analysis of \([(Et_3P)_2(CdBr_2)_2]\) showed that the molecule possessed a centre of symmetry and must, therefore, have the trans symmetric structure III.

Wymore and Bailar (191) have also assigned tetrahedral configuration to cadmium in the complex \([Cd(diphos)Br_2]\)
FIG. V-2

TGA CURVES

○ DPB CdCl₂
△ DPB Cd Br₂
□ DPB Cd I₂
Coates and Ridley (59a), while studying metal-halogen stretching frequencies in the infrared spectra of 1,2-bis(diphenylphosphino)ethane complex with cadmium(II) chloride, have observed cadmium-chlorine absorption in the region of \(260 \text{ cm}^{-1}\). This has been taken to be an indication of the existence of this complex \(\text{Cd(diphos)}\text{Cl}_2\) as individual molecules in the crystalline state. The possibility of this complex having a polymeric structure with hexa-coordinated cadmium which is the case in complexes like \((\text{NH}_3)_2\text{CdCl}_2\), \(\text{py}_2\text{CdCl}_2\), \(\text{NH}_4\text{CdCl}_3\), \((\text{NH}_4)_4\text{CdCl}_6\) and \(\text{K}_4\text{CdCl}_6\) etc. was ruled out by them because none of these complexes shows any bands above \(200 \text{ cm}^{-1}\) which could be due to \((\text{Cd-Cl})\) as shown by the complex \(\text{Cd(diphos)}\text{Cl}_2\). Nyholm and his coworkers (128) have reported the cadmium(II) halide complexes with the ditertiary arson, \(\sigma\)-phenylenebis(dimethylarsine). These complexes, which act almost as non-electrolytes in nitromethane, have been considered to contain tetrahedrally coordinated cadmium.

![Diagram](image-url)

Relative stabilities of these complexes have been discussed
with a particular reference to the relative importance of the polarizing power of the metal ion and the possibility of its forming $d_{\pi} - d_{\pi}$ bonds with the ligand. Cadmium(II) perchlorate gives bi-univalent bis-diarsine complex with the structure:

By analogy with the cadmium(II) halide complexes with monoditertiary phosphines, ditertiary phosphines and the ditertiary arsine mentioned above, it is believed that the complexes under study have a four coordinate tetrahedral configuration around cadmium and they have the chelate structure:

The infrared spectra of both the free ligands and their complexes have been examined in nujol mull. The spectra of the ligands are very rich in bands and so far no attempt has been made to make the assignments. But quite
significant feature of the spectrum is shifting of the broad 1100 cm\(^{-1}\) band in the free ligand to higher frequencies with increase in intensity and resolution into two components in the complexes. This observation is supported by Carty and Tuck (26) who have reported similar observations while studying the infrared spectra of the complexes of gallium(III) and indium(III) halides with \(1,2\)-bis(diphenylphosphino)ethane.

**Experimental**

**Dichloro \(1,2\)-bis(diphenylphosphino)ethane-cadmium(II)**

The ligand DPE (1.0 g.) was dissolved in ethanol (50 ml.) by refluxing on a water bath and cadmium(II) chloride (0.5 g.) was dissolved separately in ethanol (20 ml.). The two solutions were mixed with thorough shaking when a white complex separated out immediately. The complex was filtered, washed with ethanol and dried under vacuum. Found: Cl, 12.19, 12.04; Cd, 18.18, 18.29; P, 10.25, 10.11. \(C_{26}H_{24}P_{2}Cl_{2}Cd\) requires Cl, 12.22; Cd, 19.27; P, 10.65. Molar conductance in nitrobenzene is 1.14 ohm\(^{-1}\)cm\(^{-1}\).

**Dibromo \(1,2\)-bis(diphenylphosphino)ethane-cadmium(II)**

A solution of the ligand DPE (1.0 g.) in alcohol (50 ml.) prepared by refluxing on a water bath, was added to
a solution of cadmium(II) bromide (0.75 g.) in ethanol (20 ml.). The mixture was thoroughly shaken and the white complex was filtered, washed with ethanol and dried under vacuum.

Found: Br, 24.05, 23.97; Cd, 16.40, 16.33; P, 9.13, 8.95.

C_{26}H_{24}P_{2}Br_{2}Cd requires Br, 23.87; Cd, 16.71; P, 9.23.

Molar conductance in nitrobenzene is 1.00 ohm\(^{-1}\)cm\(^{-1}\).

**Di-iodo 1,2-bis(diphenylphosphino)ethane-cadmium(II)**

The ligand DPE (1.2 g.), dissolved in ethanol (60 ml.) by refluxing, was added to a solution of cadmium(II) iodide (1.2 g.) in ethanol (30 ml.) with thorough shaking. The white complex was filtered and washed with ethanol. It was finally dried under vacuum.

Found: I, 33.50, 33.38; Cd, 14.13, 14.04; P, 8.05, 7.89.

C_{26}H_{24}P_{2}I_{2}Cd requires I, 33.67; Cd, 14.65; P, 8.12.

Molar conductance in nitrobenzene is 1.07 ohm\(^{-1}\)cm\(^{-1}\).

**Dichloro 1,4-bis(diphenylphosphino)butane-cadmium(II)**

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

Found: Cl, 12.03, 11.89; Cd, 17.52; 17.40; P, 10.32, 10.50.

C_{28}H_{28}P_{2}Cl_{2}Cd requires Cl, 11.65; Cd, 18.43; P, 10.16.

Molar conductance in nitrobenzene is 1.01 ohm\(^{-1}\)cm\(^{-1}\).
Dibromo 1,4-bis(diphenylphosphino)butane-cadmium(II)

A solution of DPB (0.9 g.) in ethanol (60 ml.), prepared by refluxing on a water bath, was added to a solution of cadmium(II) bromide (0.8 g.) in ethanol (30 ml.) with shaking. The white complex separated out almost immediately. It was filtered, washed with ethanol and dried under vacuum. Found: Br, 22.59, 22.53; Cd, 15.13, 14.94; P, 8.58, 8.46. C_{28}H_{28}P_{2}Br_{2}Cd requires Br, 22.92; Cd, 14.23; P, 8.86.

Molar conductance in nitrobenzene is 1.02 Ohm\cdot cm^{-1}.

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

The ligand DPB (0.8 g.) was dissolved in ethanol (50 ml.) by refluxing on a water bath. This was added to a solution of cadmium(II) iodide (0.8 g.) in ethanol (25 ml.) with thorough shaking. The white complex was filtered, washed with ethanol and dried under vacuum. Found: I, 31.63; 31.52; Cd, 13.60, 13.47; P, 7.49, 7.40. C_{28}H_{28}P_{2}I_{2}Cd requires I, 32.07; Cd, 14.14; P, 7.91.

Molar conductance in nitrobenzene is 0.77 Ohm\cdot cm^{-1}.

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