INTRODUCTION
Trialkyl phosphates $R_3PO_4; R = CH_3, C_2H_5$ and $n-C_4H_9$ etc. are the esters of phosphoric acid. These are liquids with high boiling points. The physical constants of trimethyl phosphate (TMP), triethyl phosphate (TEP) and tri-n-butyl phosphate (TBP) are given in Table 1.

**Table 1**

Physical constants of trialkyl phosphates

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Property</th>
<th>TMP</th>
<th>TEP</th>
<th>TBP</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Sp. conductance $(30^\circ, \text{ohm}^{-1} \text{cm}^{-1})$</td>
<td>$3.55 \times 10^{-6}$</td>
<td>$2.35 \times 10^{-6}$</td>
<td>$2.54 \times 10^{-7}$</td>
</tr>
<tr>
<td>2.</td>
<td>Dipole moment (D)</td>
<td>3.02</td>
<td>3.07</td>
<td>2.33</td>
</tr>
<tr>
<td>3.</td>
<td>Dielectric constant $(at 25^\circ)$</td>
<td>-</td>
<td>13.0</td>
<td>8.13</td>
</tr>
<tr>
<td>4.</td>
<td>Viscosity $(at 20^\circ, \text{poise})$</td>
<td>1.3963</td>
<td>1.4053</td>
<td>1.4249</td>
</tr>
<tr>
<td>5.</td>
<td>Density $(at 20^\circ, \text{gms/cc})$</td>
<td>1.2144</td>
<td>1.0695</td>
<td>0.9766</td>
</tr>
<tr>
<td>6.</td>
<td>Boiling point $(^\circ C)$ $(62^\circ/5 \text{ mm})$</td>
<td>$62^\circ/5 \text{ mm}$</td>
<td>$112^\circ/22 \text{ mm}$</td>
<td>$140^\circ/2 \text{ mm}$</td>
</tr>
<tr>
<td>7.</td>
<td>Molecular Refraction $(20^\circ, \text{MnD})$</td>
<td>-</td>
<td>255.19</td>
<td>379.50</td>
</tr>
<tr>
<td>8.</td>
<td>Surface Tension $(\text{Dynes/cm})$</td>
<td>37.76/17.5°C</td>
<td>29.46/16.9°C</td>
<td>18.15/16.6°C</td>
</tr>
<tr>
<td>9.</td>
<td>Parachor $(285.9/17.5^\circ C)$</td>
<td>285.9/17.5°C</td>
<td>516.0/16.9°C</td>
<td>6263/16.6°C</td>
</tr>
</tbody>
</table>
The structures of trialkyl phosphates have been investigated by spectroscopic methods (1,2), vide which it has been shown that the phosphorus atom is tetrahedrally surrounded by three alkoxy groups and an oxygen atom. The structure of trialkyl phosphates may be represented as shown below:

\[ \begin{array}{c}
\text{RO} \\
\text{RO} \quad \text{P} = \ddot{\text{O}}: \\
\text{RO} \\
\end{array} \]

Fig. I

The structural aspects of organo phosphates, phosphonates and phosphinates have attracted the attention of a number of chemists due to their importance in biological processes. The structures of trialkyl phosphates, being relevant to us, shall be looked into in some detail.

The trialkyl esters of phosphoric acid can also be regarded as derivatives of phosphoryl trichloride. Although the structure of this molecule requires no description, yet it will be quite relevant to look into the various 'valence-bond structures' as these will concern us later. \( \text{POCl}_3 \) molecule has a tetrahedral structure in which the oxygen atom and the three chlorine atoms are attached to the phosphorus atom by \( \sigma \) bonds. Three \( \sigma \) bonds are reinforced by \( \pi \) interactions and the extent of dative \( \pi \) bonding varies with substituents on
phosphorus. The following four resonating structures have been sketched for the molecule (3).

\begin{align*}
  & X-\overset{\text{I}}{P}^\pm X \quad X-\overset{\text{II}}{P}^-X \quad X-\overset{\text{III}}{P}^X \quad X-\overset{\text{IV}}{P}^-X^+
\end{align*}

Fig.II

The 'orbital overlap picture' of the $\text{PCl}_3$ molecule, indicating the $\delta-\Pi$ overlap of vacant d orbitals on phosphorus and filled p orbitals on oxygen, is being reproduced here.

\begin{align*}
  & \text{Orbital overlap in the phosphoryl P-O bond}
\end{align*}

Fig.III
On a theoretical basis a similar overlap between phosphorus and chlorine atoms is not fully ruled out. But due to reasons based on symmetry considerations the P-Cl bonds get a very minor share of the dative character which is prominent in the P-O bondage. The trialkyl esters of phosphoric acid are expected to trace a similar picture of chemical bonding in them with minor modifications depending upon the substituents on phosphorus, however.

Due to the presence of lone pairs of electrons on the oxygen atom of the P-O: group the trialkyl phosphates behave as electron donors (1). Gutmann and coworkers (4) have prepared a donor scale for Lewis bases based on the enthalpies of adduct formation with SbCl₅. On this basis it has been found that the trialkyl phosphates are moderately strong donors. Thus a number of donor acceptor complexes of trialkyl phosphates with strong Lewis acids have been isolated. Boron(III) chloride, for example, forms 1:1 adducts with trialkyl phosphates (5) (Alkyl = Me, Et, Pr¹, Prᵢ, Buⁿ, Buᵢ, and n-pentyl). The addition compound, (RO)₃PO:BCl₃, is formed at temperature below 0°C and upon raising the temperature the elimination of alkyl chloride, olefin and hydrogen chloride occurs leading to the formation of a compound marked by a network of —P—0—B—0— links and it has a composition close to that of boron phosphate, BPO₄. The elimination occurs approximately in a step-wise manner. The final residue at 100°C has practically all the boron and
phosphorus in the systems except in the case of the trimethyl compound.

Trialkyl phosphates (alkyl = methyl, ethyl and n-butyl) form 1:2 adducts with tin(IV) chloride. On heating the methyl adduct for 14 hours at 80°C a compound of composition, SnCl₂[O₂P(CH₃)₂]₂ is formed. With ferric chloride TMP and TEP form addition compounds (7) of composition, [(RO)₃PO]₃[FeCl₃]₂.

Trialkyl phosphates also form charge-transfer complexes with iodine (8,9). Their formation has been supported by electronic spectra which shows a charge-transfer band at 220 nm and also there is a blue shift in the visible band of iodine from 525 nm and 450 nm. Kliegman and coworkers (8), on the basis of quantitative measurements of the intensity of the iodine band at various concentrations and temperatures, have shown that TBP forms a stable 1:1 charge-transfer complex with iodine.

\[ \text{TBP} + \text{I}_2 \rightarrow \text{TBP} \cdot \text{I}_2 \]  \( \ldots (1) \)

The \( \Delta H \) value of the reaction is -2.94 Kcal/mole and \( \Delta S \) value is -3.99 eu. The magnitude of \( \Delta H \) lies well within the range of similar complexes of iodine with ether and ethanol. Taking into account the electronic structure of TBP, it is concluded that iodine interacts mainly with the phosphoryl oxygen. It has also been found that TBP does not interact with \( \gamma' \) acceptors such as p-quinone and tri-nitrobenzene.

Triethyl phosphate is also known to form complexes with sulphur dioxide and sulphur trioxide (10). Infrared spectral
studies of these complexes have shown that coordination occurs through oxygen atom of the P=O group. The TEP-SO₃ complex has been successfully used for the sulphonation of the organic compounds.

TEP and TBP form 2:1 adducts with uranyl nitrate (11), U₂(NO₃)₂.2R₃PO₄. This has lead to the use of TBP for uranium extraction, and it has been used profitably for this purpose. Tri-n-butyl phosphate has been extensively used in solvent extraction studies (12,13,14). A large number of metals have been extracted both by pure TBP and its mixtures with carbon tetrachloride, benzene cyclohexane and hydrochloric acid. Transition and rare earth metals are extracted directly as metal cation solvates. A selective separation of selenium(IV), resulting in the composition of the extractable species, $H_{2}[SeO₃(TBP)_3]$, has been reported (15). Iron(III) and zirconium(IV) have been extracted as FeCl₃.TBP and ZrCl₄.TBP.

2,4,6-Trichloroborazine forms hydrogen bonded adducts with trialkyl phosphates (16), Cl₃B₃N₃H₃·3L, where L = TMP, TEP and TBP. These upon heating yield alkyl chloride and a solid borazole system with $-OP(0)(OR)_2$ units attached to the B atoms. At higher temperatures trialkyl phosphate is eliminated and borazole rings get attached to B atoms. At temperatures higher than 500°C further polycondensation yields infusible, hydrolytically stable inorganic polymer, containing boron, nitrogen and phosphorus.
Triethyl and tri-n-butyl phosphates have been reported to form donor-acceptor complexes with As Cl₃, viz., TEP.AsCl₃, TBP.AsCl₃ and 2TBP.AsCl₃ in solution in carbon disulphide (17). Their stability constants have also been determined in situ by Job's method. The stability constants of the complexes are as under:

\[
K_{1:1} = \frac{[\text{TEP.AsCl}_3]}{[\text{TEP}][\text{AsCl}_3]} \text{ is } 14.2 \pm 1.7 \text{ (mole/1)}^{-1}
\]

\[
K_{1:1} = \frac{[\text{TBP.AsCl}_3]}{[\text{TBP}][\text{AsCl}_3]} \text{ is } 15.4 \pm 1.6 \text{ (mole/1)}^{-1}
\]

\[
K_{2:1} = \frac{[\text{2TBP.AsCl}_3]}{[\text{TBP}]^2[\text{AsCl}_3]} \text{ is } 4.2 \pm 0.25 \text{ (mole/1)}^{-2}
\]

The stability constant in case of the 2:1 complex of TBP with As Cl₃ is very small as compared to that of the 1:1 complex.

Yoke and Schmidt (18) have been able to prepare a complete series of complexes, CoCl₂.2\left[\text{OP(C}_2\text{H}_5\right)_n(\text{OC}_2\text{H}_5)_{3-n}\left]_n \right.\text{; n = 0 to 3, which have been characterised by analysis, electronic and infrared spectroscopy. Cobalt(II) has a pseudo tetrahedral environment in these compounds. These workers have further shown that the complexes which have one or more OR groups, readily eliminate an alkyl chloride upon heating, thus yielding solvo complexes.}

\[
\text{CoCl}_2 \cdot \left[\text{OP(C}_2\text{H}_5\right)_n(\text{OC}_2\text{H}_5)_{3-n}\left]_n \right. \rightarrow 2\text{C}_2\text{H}_5\text{Cl} + \text{Co}\left[\text{O}_2\text{F(C}_2\text{H}_5\right)_n(\text{OC}_2\text{H}_5)_{2-n}\left]_n \right.
\]

... (2)
Formation of 1:2 complexes of Cobalt(II), nickel(II) and manganese(II) chlorides with TBP has been examined during the extraction of these salts by TBP (19). Triphenyl phosphate (TPP) and TBP form donor-acceptor complexes with titanium(IV) and vanadium(IV) chlorides, where vanadium(IV) disproportionates to vanadium(III) to give compounds of the type \( \text{VCl}_3 \cdot 2L \). But in case of titanium(IV) chloride compounds of composition, \( \text{TiCl}_4 \cdot 2L \) are obtained, \( L = \text{TBP, TPP} \). These complexes have been characterised by infrared and visible spectra and other physicochemical measurements.

Taube and co-workers (21) have prepared a cobalt(III) complex, triethyl phosphate-pentaaminecobalt(III) perchlorate, \( \left[ \text{Co(NH}_3\text{)}_5\text{OP(OC}_2\text{H}_5\text{)}_3 \right] (\text{ClO}_4)_3 \). The coordinated phosphate ester is more labile to substitution than is water in the same position and this complex has been used to prepare novel cobalt(III) pentaamine complexes, e.g., \( \left[ \text{Co(NH}_3\text{)}_5\text{NOCH=CH}_2 \right] (\text{ClO}_4)_3 \). Corresponding tri-n-butyl phosphate derivative is even more sensitive to substitution.

Interaction of trimethyl phosphate with metal perchlorates (22) leads to the formation of cationic complexes of the type, \( \left[ \text{M(TMP)}_6 \right]^{n+} \) \( \left( \text{M} = \text{Mg(II), Ca(II), Al(III), Cr(III)} \right) \) and \( \text{Fe(III)} \)), \( \left[ \text{Ce(TMP)}_6 \cdot 0\text{ClO}_3 \right]^{2+} \), \( \left[ \text{M(TMP)}_5 \right]^{2+} \) \( \left( \text{M} = \text{Mn, Fe, Co, Cu, Zn} \right) \) and \( \left[ \text{M(TMP)}_5\text{H}_2\text{O} \right]^{2+} \). The pentacoordinated \( \text{Mn(II)}, \text{Fe(II), Co(II)} \) and \( \text{Cu(II)} \) complexes are of high-spin type. These complexes have been characterised by means of spectral, magnetic, conductance and x-ray powder diffraction studies. A distorted \( \text{Oh} \) symmetry has been assigned to the hexacoordinated cationic complexes and a \( \text{C}_{5v} \) symmetry to the pentacoordinated complex.
cations. Solid state and solution electronic spectra are discussed and compared with those reported for complexes of organo phosphoryl esters.

The donor capability of the trialkyl esters has been exploited by Drago and coworkers (23) and they have completely shaken the solvent system concept by making a comparative study of the behaviour of ferric chloride in triethyl phosphate and phosphoryl chloride. And it has been shown that in both these solutions tetrachloroferrate ions are present. The solvent system concept fails to explain the formation of tetrachloroferrate ion in triethyl phosphate in the absence of an external chloride ion donor. However, the formation of tetrachloroferrate ion in triethyl phosphate in the absence of an external chloride ion donor. However, the formation of tetrachloroferrate ion in phosphoryl chloride can be readily explained by the following solvolytic reaction:

\[
P_0C\text{Cl}_3 \rightleftharpoons P_0C\text{Cl}_{2}^{+} + \text{Cl}^{-} \quad \ldots (3)
\]

\[
\text{FeCl}_3 + P_0C\text{Cl}_3 \rightleftharpoons \text{POCl}_3\text{FeCl}_3 \rightleftharpoons \text{POCl}_{2}^{+} + \text{FeCl}_4^{-} \quad \ldots (4)
\]

In order to explain the formation of \( \text{FeCl}_4^{-} \) in TEP Drago and co-workers (loc. cit.) have offered an alternative set of reactions where the first step involves the formation of a donor-acceptor complex which in the presence of excess of solvent undergoes solvolysis to form the tetrachloroferrate(III) ion.

\[
\text{FeCl}_3 + Y_3\text{PO} \rightleftharpoons \text{Cl}_3\text{Fe}_{.}\text{OPY}_3 \rightleftharpoons [\text{FeCl}_{3-x}.(\text{OPY}_3)_x]^{x+} + x \text{ FeCl}_4^{-}
\]

where \( Y = \text{Cl} \) or OR group and \( 0 < x \leq 3 \)
The coordination model proposed above can effectively take into account the features of ferric chloride solutions in triethyl phosphate and formation of FeCl₄⁻ observed in phosphoryl chloride and phenyl phosphoryl chloride. A comparison of the conductometric and spectrophotometric studies of ferric chloride in the phosphoryl solvents suggests that the solvent ionisation is not a primary requirement to explain equilibria and chemical reactions that occur in phosphoryl chloride and phenyl phosphoryl chloride.

From a study of the infrared spectra of donor-acceptor systems (loc. cit) it has been established that it is invariably the oxygen atom of the P=O group in trialkyl phosphates which acts as a donor atom. Since after coordination through oxygen of the P=O group the labile π electron cloud is cragged towards oxygen atom which results in a decrease in the electron density of the P=O group thus resulting in a lowering of \( \nu(P=O) \) frequency.

Recently Paul and coworkers have used trialkyl phosphates as solvents (24,25). As is evident from table 1 that the specific conductance values of TMP, TBP and TBP are very low suggesting thereby that the autoionisation in the case of these solvents is negligible. They have studied the solution of the chlorides of cobalt(II), copper(II), iron(III), arsenic(III), tin(IV), titanium(IV), antimony(V) and phosphorus(V) in TMP and those of cobalt(II), manganese(II), copper(II), boron(III), iron(III) in TBP while the chlorides of cobalt(II), manganese(II), copper(II), iron(III), silicon(IV), tin(IV), titanium(IV), antimony(V) and phosphorus(V) have been
studied in TBP. It is observed that the addition of these compounds in trialkylphosphates is followed by an appreciable increase in the conductance of the solution. This suggests dissociation of the chlorides in dilute solutions. Phosphorus(III) and silicon(IV) chlorides remain unionized in these solvents. At higher molar-ratios of the chlorides the increase in conductance is relatively low and the formation of addition compounds of general stoichiometry, $\text{MCl}_n\text{aOPY}_3$ ($Y = \text{OC}_3\text{H}_7, \text{OC}_2\text{H}_5, 0-\text{n-C}_4\text{H}_{2n}$) have been indicated. The equilibria in solution have been explained on the basis of coordination model as shown below:

$$\text{MCl}_n + \text{aOPY}_3 \rightarrow \text{MCl}_n\text{.aOPY}_3 \quad \ldots(6)$$

$$\text{MCl}_n\text{.aOPY}_3 + m\text{OPY}_3 \rightarrow [\text{MCl}_{n-x}(\text{OPY}_3)_{a+m}]^{x+} + \text{XCl}^- \quad \ldots(7)$$

$$\text{MCl}_n\text{.aOPY}_3 + \text{XCl}^- \rightarrow [\text{MCl}_{n+x}]^{x-} + a\text{OPY}_3 \quad \ldots(8)$$

The formulations based on coordination model have also been supported by conductometric study of the solution-equilibria in the presence of tetraethylammonium chloride (or lithium chloride) and pyridine.

The integral heats of reactions, $\Delta H$, of chlorides of cobalt(II), manganese(II), copper(II), iron(III), aluminium(III), titanium(IV), tin(IV), antimony(V), phosphorus(III) and iodine(III) and of thionyl chloride and phosphoryl(V) trichloride, in TBP have been measured calorimetrically (24). $\Delta H$ decreases in the following order:

$\text{TiCl}_4 > \text{SbCl}_5 > \text{SnCl}_4 > \text{FeCl}_3 > \text{AlCl}_3 > \text{MnCl}_2 > \text{CuCl}_2 > \text{CoCl}_2 > \text{PCL}_3 > \text{POCl}_3 > \text{SOCl}_2 > \text{ICl}_3$. 
Nucleophilicities of trialkyl phosphates are slightly more than those of ethanol, water, ethers or ketones (3). However, under varying conditions, these compounds behave both as nucleophiles and electrophiles. Both types of reactions (the one in which bond between phosphorus and oxygen is broken and the other in which bond between carbon and oxygen is broken) have been studied in detail. It has been shown that trialkyl phosphates are hydrolysed in the basic solution to the corresponding diesters by means of an associative mechanism forming the following species in the transition state (27):

\[
\begin{align*}
\text{Fig. IV} \\
\text{(Y = OH}^-, \text{OMe}^-) \\
\end{align*}
\]

Another important and interesting feature of the chemistry of trialkyl phosphates is the formation of dialkoxyphosphato chelates. It has been shown by Gutmann and coworkers (28) and later by other workers (18,29) that a metal halide (chloride/bromide) reacts with trialkyl phosphates to yield metal chelates with the elimination of an alkyl halide.

The reaction is summarised as under:

\[
\text{nP(OR)₃ + MX}_n \rightarrow \text{M[O}^\text{*}_2\text{P(OR)}_2\text{]}_n + \text{nRX} \quad \ldots(9)
\]

where \( \text{O}^\text{*} \): chelating oxygen atoms
Mikulski and coworkers (30) have reported a number of such chelates with chlorides of non-transition metals.

Scope of the Present Work:

The survey of literature shows that a very large number of donor-acceptor compounds of trialkyl phosphates have been prepared, signifying the donor character of the $\overset{\rightarrow}{P}=O$ group. But detailed investigations have not been carried out on the formation and characterization of metal chelates as suggested in equation (9) above. The present dissertation deals with this aspect of the chemistry of trialkyl phosphates. From equation (9) it is apparent that a divalent metal ($n=2$) shall give rise to a four coordinate metal chelate while a trivalent metal ion ($n=3$) should bring forth a hexa-coordinated system. The divalent transition metal ions of the first transition series are known for their behaviour to acquire a coordination number of six. Attempts have been made to expand the coordination polyhedron of the divalent metal chelates, formed by trialkyl phosphates, by 'pushing in' strong nitrogen donors.

The thesis has been broadly apportioned into four chapters:

(i) Diethoxyphosphato chelates of some first transition series elements (31,32)*.

(ii) Studies on the interaction of Bis(dialkoxyphosphato) cobalt(II) chelates with Lewis bases in solution (33,34,35)*.

(iii) Characterisation and isolation of the complexes of $M\left[\overset{\rightarrow}{O_2P(OR)}\right]_2\cdot2B$ (33,36)*.

where $M = \text{Co(II)}, \text{Ni(II)}$

$B = \text{H}_2\text{O}$ and nitrogen donors

*Reprints attached
(iv) Bis(dialkoxyphosphato) chelates as donors (37)*

The following physicochemical/ spectral studies have been made to throw light on the structure etc. of the complexes prepared.

(i) Conductivity measurements
(ii) Infrared spectra
(iii) Electronic spectra
(iv) Magnetic susceptibility measurements.