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Alkylene Diphosphine Dioxides as Extractants and Complex-forming Agents

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Alkylenediphosphine dioxides are a new group of highly effective complex-forming agents capable of binding metal ions to form chelate rings. The review discusses methods for the synthesis of neutral bidentate organophosphorus complex-forming agents based on diphosphine dioxides, their extraction properties, and the possibility of the modification of the structural and steric factors which influence significantly the complex-forming properties of the ligand.
The bibliography includes 133 references.

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1. INTRODUCTION

One of the characteristic properties of organic compounds of phosphorus is their ability to form complexes with metal ions. The study of these properties of organophosphorus compounds is not only of theoretical interest but also leads to the solution of many important practical problems.

Extensive study of the complex-forming properties of organic derivatives of quinquevalent phosphorus was stimulated by the development of the atomic energy industry which gave rise to a vigorous search for methods whereby complex mixtures of metals could be separated. Compounds containing P=O bonds proved to be highly effective for this purpose. Since then organophosphorus compounds, mainly phosphates, have been widely used in technology as extractants with isolation and concentration of metals.

Further development and improvements in this field have proceeded on lines designed to create more effective complex-forming agents, more selective with respect to individual groups of metal ions, and more universal in their applications. All these problems are now of urgent importance owing to the rapid development of technology and analytical chemistry.

Among the neutral organophosphorus complex-forming agents containing phosphorus(V) which have now been investigated tertiary phosphine oxides exhibit the greatest complex-forming capacity. Their effectiveness greatly exceeds that of phosphates, phosphonates and phosphinates. Although the ability of phosphine oxides to form complexes varies as a function of their structure and the nature of the substituents at the phosphorus atom, the variation do not exceed significantly an order of magnitude.

Fundamentally different possibilities of improving the effectiveness and selectivity of the complex-forming phosphine oxides arise when the chelate-forming effect is used. For this purpose, it is necessary to have substances containing in the molecule at least two and possibly more phosphine oxide groups, when the complex-forming capacity can be enhanced as a result of the formation of rings with the metal ions involving two or several phosphoryl groups.

One of the new trends in the field of organophosphorus complex-forming agents in fact constitutes the synthesis of substances with the structure of polydentate ligands. This group of substances is of interest also because it gives rise to extensive possibilities for the modification of the structural and steric factors which influence significantly the complex-forming properties of the ligands.

In 1968 Kabachnik et al.[1] published a review on the methods of synthesising organophosphorus complexones and their complex-forming properties. This paper is devoted to neutral bidentate organophosphorus complex-forming agents based on alkylenediphosphine dioxides† and consists of two parts: the first discusses the method of synthesising compounds of this class and the second deals with data on their extraction and complex-forming properties; the problems concerning the derivation of a relation between the extraction and complex-properties of polydentate ligands and their structure have been combined in a separate section.

2. METHODS OF SYNTHESIS

a. The Arbuzov Reaction

This classical method of organophosphorus synthesis has been extensively used recently to obtain a wide variety of tertiary alkylenediphosphine dioxides. When a phosphine oxide containing a chloromethyl group is allowed to react with an ester of a secondary phosphinous acid, the dioxide of the tetrasubstituted methylenediphosphine is formed:

$$Ph_2P(O)-CH_2Cl + Ph_2P-OEt \rightarrow Ph_2P(O)-CH_2-PPh_2(O)$$

Tetraphenylbenzylidenediphosphine dioxide was synthesised similarly from α-chlorobenzyldiphenylphosphine oxide and ethyldiphenylphosphinite[4]. Derivatives of tetraphenylmethylenediphosphine with various substituents in

† We shall not consider the esters of alkylenediphosphonic acids, since a special review has been devoted to substances of this class[2].

the *meta*- and *para*-positions in the phenyl group were synthesised in the same way[5]:

$$(XC_6H_4)_2P(O)-CH_2-P(O)(C_6H_4X)_2,$$

where X = CH_3, CH_3O, Cl, Br, or CF_3.

The method of synthesising methylenediphosphine dioxides was extended to polymethylenepolyphosphine polyoxides, i.e. compounds containing several $-P(O)-CH_2-P(O)-$ units in the molecule[6-11]. The oxides of tertiary di(chloromethyl)-phosphine and tri(chloromethyl)-phosphine were introduced into the reaction with phosphorus(III) acid esters. In the first case the reaction proceeds via the mechanism

$$R-P(O)(CH_2Cl)_2 + 2EtOP(R')(R'') \rightarrow R''(R')P(O)-CH_2-P(O)(R)-CH_2-P(O)(R')(R'') .$$

The intermediate products of the incomplete interaction of the initial components, $R'R''P(O)-CH_2-P(O)(R)CH_2Cl$, were also isolated.

The condensation of tri(chloromethyl)phosphine oxide with three ester molecules proceeds similarly:

$$(ClCH_2)_3P=O + 3EtO-P(R')(R') \rightarrow (R'R''PCH_2)_3P=O .$$

Compounds with R = CH_3, C_2H_5, $C_{12}H_{25}$, C_6H_5, C_2H_5O, or C_4H_9O and R′ and R″ = C_4H_9 or C_6H_5 were obtained.

Thus the chloromethyl group at the phosphorus atom, which contains a relatively passive halogen atom, is fairly reactive as regards the isomerisation of phosphorus(III) acids, which can be used successfully for the synthesis of a wide variety of polymethylenepolyphosphine polyoxides.

In the synthesis of ethylenediphosphine oxides one can employ as starting materials the β-chloroethyl esters of dialkyl- or diaryl-phosphinous acids, which on heating give rise to two products of the Arbuzov rearrangement; β-chloroethylphosphine oxide and ethylenediphosphine dioxide[12,13]:

$$R_2P-O-C_2H_4Cl \xrightarrow{t^\circ} R_2P(O)C_2H_4Cl \quad R_2P(O)C_2H_4P(O)R_2 .$$

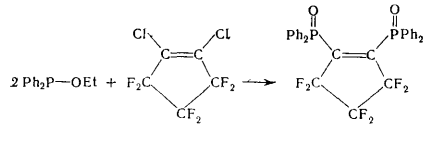
Depending on the conditions, the reaction proceeds preferentially via one pathway or the other. Thus isomerisation in solution promotes the formation of the monoxide and hinders the formation of the diphosphine dioxide. Presumably the β-chloroethyl ester of phosphinous acid initially undergoes intramolecular or intermolecular isomerisation and the resulting β-chloroethylphosphine oxide reacts like an alkyl halide with a second molecule of the β-chloroethyl ester via the mechanism of the Arbuzov rearrangement.

Diphosphine dioxides with ethylene and propylene bridges between the phosphorus atoms have been obtained from phosphinite esters and the corresponding dihalogenoalkanes[14]:

$$2(PhCH_2)_2P-OEt + Br(CH_2)_nBr \rightarrow (PhCH_2)_2P(O)-(CH_2)_n-P(O)(CH_2Ph)_2 .$$

(n = 2 and 3)

The reaction[15]



proceeds similarly.

In the above examples the Arbuzov isomerisation was used to bind two phosphorus-containing residues into the molecules of the alkylenediphosphine dioxide. The latter are also formed in the isomerisation of diphosphinous acid esters. For example, the Arbuzov rearrangement of a 1,4-dialkyl-substituted tetramethylenebis(diphenylphosphinite) in the presence of ethyl iodide leads to the formation of a tetraphenylalkylenediphosphine dioxide:

$$Ph_2-P-O-CHRCH_2CH_2CHR-O-P-Ph_2 \rightarrow Ph_2P(O)-CHRCH_2CH_2CHR-P(O)Ph_2 .$$

When the product of the reaction of ethylene glycol with chlorodiphenylphosphine is distilled, tetraphenylethylenediphosphine dioxide is formed immediately[16]. $Ph_2P(O)CH_2-CHPhOPPh_2$ also rearranges readily[17].

Alkylenediphosphine dioxides are also formed when phosphinamides react with diols with subsequent isomerisation on heating in the presence of catalytic amounts of dibromoethane[18]:

$$2R_2PNR'_2 + HO(CH_2)_nOH \rightarrow R_2P(O)-(CH_2)_n-PR_2(O) ,$$

where R = C_2H_5, C_4H_9, or C_6H_5 and n = 2, 3, 4, or 12.

b. The Michaelis–Bekker Reaction

The use of the magnesium salts of phosphorus(III) acids for the synthesis of alkylenediphosphine oxide was investigated by Kosolapoff[19]. The dioxides of tertiary alkylenediphosphines can be obtained in low yields by the reaction of halogenomagnesium salts of phosphinous acids with alkylenebis(toluene-*p*-sulphonates):[20]

$$2(Ph_2)POMgHal + Tos-O(CH_2)_nO-Tos \rightarrow Ph_2P(O)-(CH_2)_n-PPh_2(O) \quad (n=2, 3) .$$

In the synthesis of tetrahexylethylenediphosphine and tetrahexylpropylenediphosphine dioxides Mrochek and Banks modified somewhat the method of isolating the product and increased the yield of the dioxide; or they also obtained tetrahexylbutylenediphosphine dioxide[21].

Tetraphenylmethylenediphosphine dioxide was synthesised by Kosolapoff and Struck[20] by treating halogenomagnesium phosphinite with methylene iodide or chloromethyldiphenylphosphine oxide[20]:

$$2Ph_2POMgCl + CH_2I_2 \rightarrow Ph_2P(O)-CH_2-PPh_2(O)$$
$$Ph_2POMgCl + ClCH_2PPh_2(O) \rightarrow Ph_2P(O)-CH_2-PPh_2(O) .$$

Strunin et al.[22] and Kabachnik et al.[23] showed that halogenomagnesium salts of phosphinous acids, obtained by the reaction of organomagnesium compounds with dialkyl phosphites, react with alkylene dihalides, yielding alkylenediphosphine dioxides:

$$2R_2POMgX + X-(CH_2)_n-X \rightarrow R_2P(O)-(CH_2)_n-PR_2(O) ,$$

where R = C_6H_5, C_6H_{13}, or C_7H_{15}, X = Cl or Br, and n = 3 or 4.

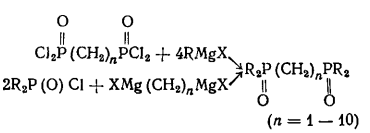
Hays[24] achieved the alkylation of the halogenomagnesium salt of dimethylphosphinous acid with 1,2-dichlorobutane[24]:

$$2Me_2POMgBr + ClCH_2CHClCH_2Me \rightarrow Me_2P(O)-CH_2-CH(Et)-PMe_2(O) .$$

Tetracyclohexylethylenediphosphine dioxide was obtained by the reaction of sodium dicyclohexylphosphinite with dichloroethane[25].

c. Syntheses using Organometallic Compounds

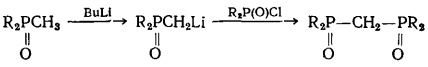
Alkylenediphosphine dioxides can be obtained by the reaction of alkylenediphosphonic acid tetrachlorides with an excess of a Grignard monoreagent[26-29] or via the reaction of a phosphinic acid chloride with a Grignard direagent[30,31]:



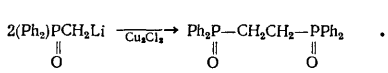
$(n = 1 - 10)$

In particular, dioxides with heteroatoms (O, S, and N) in the alkylene bridge between the phosphorus atoms were obtained in this way[26].

Richard and Banks described the synthesis of methylenediphosphine dioxides with symmetric and asymmetric structures from the lithio-derivatives of phosphine oxides and phosphinic acid chlorides[32]:

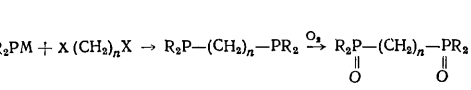


Tetraphenylethylenediphosphine dioxide is formed when the molecules of the lithio-derivative of methyldiphenylphosphine oxide are dimerised under the influence of copper(I) chloride in tetrahydrofuran with subsequent treatment of the reaction mixture with oxygen[33]:



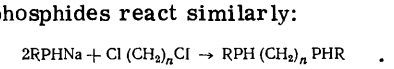
d. Syntheses based on Alkali Metal Phosphides

Certain syntheses of alkylenediphosphine dioxides involve the use of alkali metal phosphides, the properties and reactions of which have been extensively studied by Issleib[34]. Their reactions with dihalogenoalkanes can yield alkylenediphosphines, whose oxidation leads to the formation of alkylenediphosphine dioxides[35-37] (for $n = 1$ or 2, the dioxides are formed only from diphenylphosphide; in other cases diphosphyls were obtained[38]):

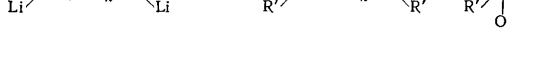


where R = C_2H_5, C_6H_{11}, or C_6H_5, $n = 1-6$, and M = Na or K.

Primary phosphides react similarly:

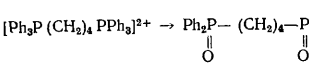


The secondary alkylenediphosphines obtained in this way were converted by metallation into dilithioalkylene diphosphides, the interaction of which with alkyl halides followed by oxidation leads to the dioxides of mixed tertiary alkylenediphosphines[39,40]:

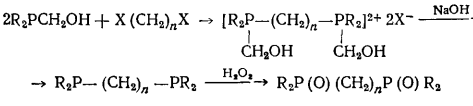


e. Cleavage of Phosphonium Salts

The formation of a butylenediphosphine dioxide from a diphosphonium salt on treatment with an excess of sodium butoxide has been described[41]:



Petrov et al. synthesised the dioxides of tertiary diphosphines by alkylating dialkyl(aryl)(hydroxymethyl)-phosphines with dihalogenoalkanes and subsequent dehydroxymethylation of the resulting diphosphonium salts with sodium hydroxide and the oxidation of the alkylenediphosphines formed[42]:

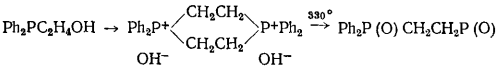


The starting materials used were diheptyl-, dibutyl-, and diphenyl-(hydroxymethyl)phosphines, methylene iodide, and 1,2-dibromoethane; the yields of the alkylenediphosphine dioxides were high.

Horner et al. obtained the dioxides of tetraphenylalkylenediphosphines by heating chlorodiphenylphosphine with $Br(CH_2)_nBr$, where $n = 2$, 3, 4, or 6, or with $ClCH_2C_6H_4.CH_2Cl$ and subsequent hydrolysis of the intermediate alkylenebis(dihalogenophosphoranes).[43]

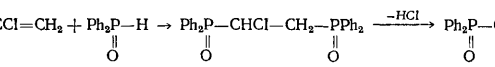
Similar syntheses was achieved by Tsivunin and Kamai and their coworkers from chlorodiethylphosphine; apart from dibromoalkanes, dichloromethyl ether was introduced into the reaction[44]. Tetramethylmethylenediphosphine dioxide was obtained from chlorodimethylphosphine and dibromomethane with subsequent decomposition by butyl alcohol[45].

Pyrolysis of (2-hydroxyethyl)diphenylphosphine leads to the formation of tetraphenylethylenediphosphine dioxide, probably via an intermediate dimeric diphosphonium base[46]:



f. Reactions Involving the Addition of Organophosphorus Compounds with a P–H Group to Multiple Bonds

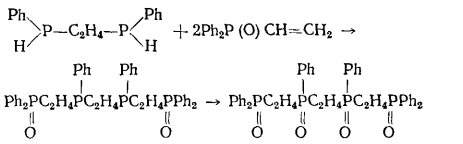
Organophosphorus compounds with a mobile hydrogen atom attached to a multiple bond have been used successfully to synthesise alkylene derivatives with two phosphorus atoms. The addition of diphenylphosphine oxide to diphenylvinylphosphine oxide leads to $Ph_2P(O)C_2H_4P(O)Ph_2$.[47] The reaction with α-chlorovinyldiphenylphosphine oxide proceeds via the following mechanism[4]:



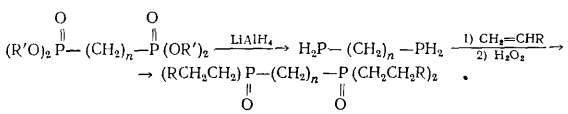
After dehydrochlorination, the *trans*-isomer of diphosphine dioxide is formed in this case (the *cis*-isomer was synthesised from Ph_2PLi and *cis*-dichloroethylene with subsequent oxidation[48]).

Alkylenediphosphines can be used as the bifunctional nucleophilic components in addition to an activated double bond. Hexaphenyltriethylenetetraphosphine tetroxide was

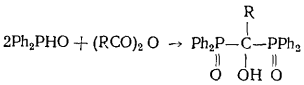
obtained by the reaction of ethylenediphenyldiphosphine with diphenylvinylphosphine oxide and subsequent oxidation[49]:



Maier[50] achieved the synthesis of alkylenediphosphine dioxides reducing alkylenediphosphonate esters to primary alkylenediphosphines with their subsequent addition to olefins and oxidation:



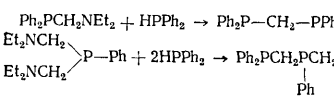
Davidson et al. described the reaction of diphenylphosphine oxide with carboxylic acid anhydrides, which apparently proceeds via a stage involving the addition of phosphine oxide to the C=O bond[51]:



where R = CH_3 or $C_6H_5CH_2CH_2$. The resulting hydroxyalkylidenediphosphine dioxides readily isomerise on heating via a mechanism of the type of the phosphonate–phosphate rearrangement.

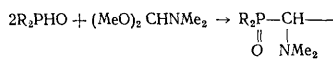
g. Other Methods

An interesting method for the formation of the P–C–P bond system was proposed by Maier on the basis of the reaction of phosphines containing the aminomethyl group with secondary phosphines[52]:



The oxidation of the products leads to the corresponding di- and tri-oxides.

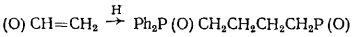
Gross and Costisella achieved the synthesis of the dioxides of amino-substituted methylenediphosphines by the reaction of the acetal or thioacetal of dimethylformamide with secondary phosphine oxides[53–56]:



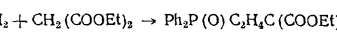
where R = C_4H_9 or C_6H_5.

Certain syntheses of the dioxides of tertiary alkylenediphosphines applicable in specific instances have been described.

Tetraphenylbutylenediphosphine dioxide has been obtained by the reductive dimerisation of diphenylvinylphosphine oxide (in aqueous acetonitrile with a platinum anode and a mercury cathode)[57]:

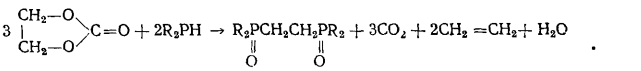


The interaction of malonic ester with two moles of diphenylvinylphosphine oxide proceeds as follows[47]:



Tetraphenylmethylenediphosphine dioxide has been obtained by the alkaline hydrolysis of methylenebis(diphenylphosphine-*N*-phenylimide)[58].

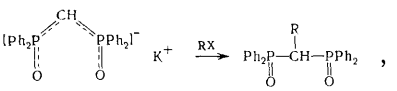
The formation of ethylenediphosphine dioxides has been observed in the reaction of dialkyl- and diaryl-phosphines with cyclic carbonic acid esters[59]:



h. Reactions of Alkylenediphosphine Dioxides

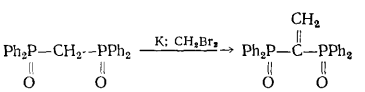
The reactions of diphosphine dioxides leading to changes in the hydrocarbon groups attached to the phosphorus atoms and proceedings without the dissociation of the C–P bonds, i.e. with retention of the initial structure of the tertiary alkylenediphosphine dioxide, are known.

Methylenediphosphine dioxides readily form metal salts on treatment with alkali metals or their hydrides. These salts are highly reactive and are used to obtain various derivatives substituted in the methylene bridge. Alkylation of the potassium salt of tetraphenylmethylenediphosphine dioxide by alkyl halides yielded *C*-alkylated products with substituents in the methylene group[60]:

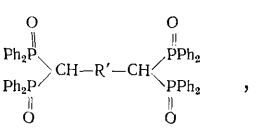


where R = C_2H_5, C_4H_9, C_6H_{13}, $C_{12}H_{25}$, $CH_2{=}CHCH_2$, or $CH{\equiv}CCH_2$.

The analogous reaction of tetraphenylmethylenediphosphine dioxide with methylene bromide leads to vinylidenediphosphine dioxide, which is probably formed as a result of the dehydrobromination of the bromomethyl-substituted dioxide by the initial potassium salt:



In the alkylation of the potassium salt of tetraphenylmethylenediphosphine dioxide by carbon tetrachloride, tetraphenyldichlorovinylidenediphosphine was obtained. The reaction of this salt with 1,6-dibromohexane and *p*-xylylene dibromide yields the corresponding octaphenylalkylenetetraphosphine tetroxides[60]:

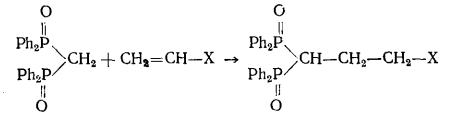


where R′ = $(CH_2)_6$ or n-$CH_2C_6H_4CH_2$.

The reaction with 1,5-dibromopentane under these conditions results in the formation of tetraphenylcyclohexylidenediphosphine dioxide.

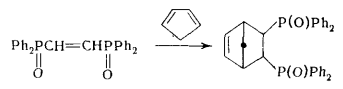
Halogenation of tetraphenylmethylenediphosphine dioxide with bromosuccinimide and thionyl chloride in the presence of azoisobutyronitrile yielded the corresponding monohalogeno-products; when the potassium salt of the dioxide is treated with iodine, the iodo-product is formed[61].

Tetraphenylmethylenediphosphine dioxide undergoes the Michael reaction in the presence of alkaline agents: its addition to ethyl acrylate, diphenylvinylphosphine oxide, and diethyl vinylphosphonate has been achieved[61]:

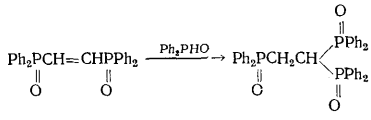


where X = C_2H_5OCO, $(C_6H_5)_2P(O)$, or $(C_2H_5O)_2P(O)$.

The *cis*- and *trans*-isomers of tetraphenylvinylenediphosphine dioxide undergo the Diels–Alder reaction with cyclopentadiene and are converted into the corresponding stereoisomers of norbornenylenediphosphine dioxide[62]:



The addition of diphenylphosphine oxide to phenylvinylenediphosphine dioxide leads to the trioxide of hexaphenyl-1,1,2-ethylenetriphosphine (which is also formed when Ph_2PHO reacts with trichloroethylene in the presence of triethylamine)[4]:



Tetracyclohexylmethylenediphosphine has been obtained by the hydrogenation of tetraphenylmethylenediphosphine dioxide over a platinum catalyst[63].

3. EXTRACTION PROPERTIES

The first reports of studies on polydentate neutral organophosphorus complex-forming agents dealt with tetraalkyl esters of alkylenediphosphonic acid[64]. Although compounds of this type are not in fact considered in this review, it is nevertheless useful to mention briefly certain investigations of their extraction properties, since relations common to alkylenediphosphine dioxides operate here too.

The study of the extraction of zirconium, yttrium, and certain lanthanides by tetra-n-butyl ethylenediphosphonate revealed its high extraction capacity[65]. Similar results were obtained in the extraction of thorium and uranium nitrates[66]. Siddal[67], who studied the properties of tetrabutyl alkylenediphosphonates $(BuO)_2P(O)-(CH_2)_n-P(O).(OBu)_2$, where n = 1, 2, 3, or 4, in the extraction of cerium, promethium, and americium, concluded that the bidentate compounds capable of forming chelates with metals (six- and seven-membered rings) are effective extracting agents.

A series of subsequent studies were devoted to the investigation of the compositions and structures of the complexes in the extraction of various metal salts by alkylenediphosphonate esters[68–73]. A common feature of all the studies quoted above is the conclusion that bidentate organophosphorus extractants have significantly more effective extraction properties (the partition coefficients are higher by a factor of 10–100) [67] than the monodentate extractants.

In the subsequent search for new highly effective neutral extractants, tetraalkyl(aryl)alkylenediphosphine dioxides were of considerable interest. These compounds have been attracting increasing attention: mainly the extraction of uranium from nitrate, chloride, and perchlorate solutions has been studied as well as the extraction of lanthanide and certain other elements. The mechanism of the extraction has been studied simultaneously with the aid of various physicochemical methods.

a. Extraction of Acids and Water

A number of investigations have been made[74–77] of the extraction of acids in which a relation between the extraction capacity of tetra-n-hexylalkylenediphosphine dioxides having the general formula $(C_6H_{13})_2P(O)-(CH_2)_n-P(O).(C_6H_{13})_2$, where n = 1, 2, 3, or 4, and the length of the hydrocarbon bridge between phosphoryl group was discovered.

Mrochek and Banks[75], who studied the extraction of nitric, hydrochloric, and perchloric acids at different concentrations with 0.05 M solutions of tetra-n-hexylalkylenediphosphine dioxides in 1,2-dichlorobenzene, showed that, with increase of the length of the hydrocarbon bridge, the extraction capacity of the dioxides increases in all cases. The degree of extraction of acids decreases in the following sequence as a function of the nature of the anion: $NO_3^- > ClO_4^- > Cl^-$.

The mechanism of the extraction of nitric acid by solutions of tetra-n-hexylmethylenediphosphine dioxide in benzene[76,77] and in carbon tetrachloride with formation of adducts has been studied most thoroughly:

$$H^+ + NO_3^- + S \overset{\bar{K}_1}{\rightleftarrows} HNO_3 \cdot S \ ,$$

$$[HNO_3 \cdot S] + H^+ + NO_3^- \overset{\bar{K}_2}{\rightleftarrows} (HNO_3)_2 \cdot S \ ,$$

where S is the extractant molecule. The effective extraction constants have been determined ($\bar{K}_1$ = 4.9 in CCl_4 and 9.8 in benzene and $\bar{K}_2$ = 0.18 and 0.35 in the two solvents respectively); with increase of the length of the bridge to n = 5, the constants become appreciably greater: $\bar{K}_1$ = 51 and $\bar{K}_2$ = 6.2.[76] However, it has been shown[77] that these equations to not describe the process fully: the constant $\bar{K}_1$ increases with increase of the extractant concentration above 0.05 M and also with decrease of the acid concentration. It has been suggested that this can be accounted for by the formation of solvates $HNO_3.mS$, where $m > 2$.

As for tri-n-butyl phosphate[78,79] and tri-n-butylphosphine oxide[80], in extraction from concentrated solutions the HNO_3 concentration in the organic phase exceeds the value for the stoichiometric composition $(HNO_3)_2.S$. Following Kertes and Platzner[81], the authors explained this by the extraction of undissociated acid.

The extraction of water by solutions of tetra-n-hexyl-, tetra-(2-ethylhexyl)-, and tetra-(3,3-dimethylbutyl)-alkylenediphosphines has been studied in chloroform[82,83] and it has been shown that complexes with water (monohydrates and dihydrates) are formed as a function of the length of the alkylene bridge in the ligand. This process competes with the extraction of salts and acids by the above compounds. Data for the distribution of water, obtained in the study of the infrared and NMR spectra, and the changes in the vapour pressure over the solutions established that, at concentrations of tetra-n-hexylmethylenediphosphine dioxide less than 0.02 M, the monohydrate is formed in the

organic phase. With increase of the extractant concentration in the organic phase, association complexes with a greater number of water molecules are produced.

b. Extraction of Uranium(VI)

The first studies in this field dealt with tetrabutyl methylenediphosphonate and tetrabutylethylene diphosphonate.

The series of studies by Banks and coworkers[74,75,82,84,85] were devoted to the investigation of a number of tetra-n-alkylalkylenediphosphine dioxides having the general formula $(Alk)_2P(O)(CH_2)_n(O)P(Alk)_2$, where $n = 1$, 2, 3, or 4. The n-hexyl, cyclohexyl, and 2-ethylbutyl substituents at the phosphorus atom were investigated. The results of the extraction of uranium(VI) and certain lanthanides from salt solutions in organic acids showed that these compounds are highly effective extractants, superior to the analogous phosphine monoxides.

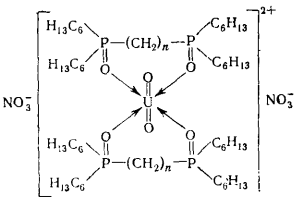
The extraction properties of tetraoctylethylenediphosphine dioxide in relation to uranyl nitrate were investigated by Laskorin and coworkers[86,87], who found that the extraction properties of this reagent depend in a complex manner on the composition of the aqueous phase.

The number of extractant molecules in the complex with uranyl nitrate has been determined[74] on the basis of the relation between the partition coefficients of uranium and the concentration of tetra-n-hexylmethylenediphosphine dioxide (S). It was found that the number is variable and depends on the ratio of the concentrations of the extractant and the salt. Thus, for equilibrium concentrations of the free extractant greatly exceeding the analogous concentration of the salt being extracted, the complex having the composition $UO_2(NO_3)_2.2S$ is formed in the organic phase. Under conditions close to saturation of the extractant, where the equilibrium concentration of the salt in the aqueous phase exceeds the equilibrium concentration of the free extractant, the complex $UO_2(NO_3)_2.S$ exists in the organic phase.

Analogous conclusions were reached in another study[85] where data were obtained, by a method involving the dilution of the extractant, for the compositions of the uranyl nitrate complexes with a number of alkylenediphosphine dioxides in solutions in 1,2-dichlorobenzene. The tetra-n-hexylalkylenediphosphine dioxides $(C_6H_{13})_2P(O)(CH_2)_n.(O)P(C_6H_{13})_2$ with $n = 1$ (DOHM), $n = 2$ (DOHE), $n = 3$ (DOHP), and $n = 4$ (DOHB) were investigated.

Examination of saturation and conductimetric data for solutions of alkylene diphosphine dioxides in 1,2-dichlorobenzene together with their infrared spectra for different ratios of the extractant and uranyl nitrate made it possible to determine the compositions and structures of the complexes extracted[85]. Thus the presence of the monosolvate $UO_2(NO_3)_2.S$ (the absorption band due to the P=O stretching vibrations is at 1136 cm^{-1}) and of the disolvate (the band at 1119 cm^{-1}) has been established for DOHM; similar solvates are also formed with DOHE (the 1124 and 1108 cm^{-1} bands).

The authors concluded that one or two NO_3^- groups in the disolvate with DOHM and DOHE are in the outer coordination sphere of the complex. This is confirmed by the greater intensity of the band due to the double degenerate antisymmetric stretching vibrations of the NO_3^- group (ν_3) at 1350 cm^{-1}, which is characteristic of the NO_3^- anion (D_{3h} symmetry) and by the sharp decrease of the intensity of the bands due to the allowed antisymmetric stretching vibrations at 1481–1520 cm^{-1} (ν_{3b}) and 1253–1290 cm^{-1} (ν_{3a}), which are characteristic of the covalently linked NO_3 group (C_{2v} symmetry)‡. Accordingly the disolvates with DOHM and DOHE have the following structure:

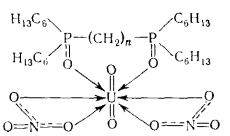


where $n = 1$ or 2.

The above data have been appreciably supplemented by studies on the structure of crystalline complexes of tetra-(2-ethylbutyl)methylenediphosphine (DOEBM) and tetracyclohexylmethylenediphosphine (DOCHM) dioxides with uranyl nitrate and thorium nitrate[84]. According to elemental analysis, the composition of the complexes isolated in the two cases is 1 : 1.

By analogy with the formation of complexes by uranyl nitrate with monodentate neutral organophosphorus compounds and bearing in mind that in the complexes with phosphate the NO_3^- group behaves as a bidentate ligand[88,96,97], the authors concluded that the NO_3 group plays a similar role in the complexes $UO_2(NO_3)_2.DOEBM$ and $UO_2(NO_3)_2.DOCHM$. This is in full agreement with the results of Mrochek et al.[85]

On passing to monosolvates, the nitrate ion anion virtually vanishes; accordingly the following structure has been attributed to the monosolvates $UO_2(NO_3)_2.DOHM$ and $UO_2(NO_3)_2.DOHE$:



where $n = 1$ or 2.

The infrared spectra of the complexes of DOHM and DOHE with uranyl nitrate, which are formed when the two reactants are in equimolar proportions, indicate the absence of water molecules from the coordination sphere of the complexes. In the spectra of the complexes where the ratio of the extractant and uranyl nitrate is 2 : 1 there is a band at 1620 cm^{-1} (O–H deformation vibrations), which indicates the presence of water molecules in their structure.

A very important result of the study of Mrochek et al.[74] is the demonstration of the bidentate coordination of uranyl nitrate to DOEBM and DOCHM on the basis of an investigation of the ^1H NMR spectra of the pure extractants and their complexes with uranyl nitrate. In the NMR spectra of solutions of DOEBM in $CDCl_3$ and of DOCHM in CCl_4 the protons of the methylene bridge give rise to a triplet, which indicates the equivalence of the two phosphorus atoms. When non-equivalent phosphorus atoms are present, as for example, in the di-(n-heptylphosphinyl)methylenephosphonic acid molecule $(n\text{-}C_7H_{15})_2P(O)CH_2(O)P(OH)_2$ the protons of the methylene bridge gave rise to a quartet signal. The fact that in the complexes $UO_2(NO_3)_2.DOEBM$ and $UO_2(NO_3)_2.DOCHM$ the protons of the CH_2 group give

‡ The infrared absorption bands of the NO_3 group under conditions where its covalent or ionic bond predominates in various compounds have been assigned in a number of studies[88–95].

rise to a triplet demonstrates the equivalence of the two phosphorus atoms and hence the bidentate coordination of the phosphoryl group.

The influence of certain electronic and steric factors on the extraction of uranium by tetraarylalkylenediphosphine dioxides has been studied. The results of these investigations are discussed below (see Section 5).

c. Extraction of Other Elements

The extraction of other elements by tetraalkyl(aryl)-alkylenediphosphine dioxides has also been investigated. The results characterise the selective properties of these substances. The qualitative data obtained by Parker and Banks[98] for the extraction of a number of elements from nitric and hydrochloric acids solution by tetra-n-hexylmethylenediphosphine dioxide are presented in the Table.

Characteristics of the extraction of a number of elements from nitric and hydrochloric acid solutions by $[n\text{-}C_6H_{13})P.(O)]_2CH_2$.

Medium	Quantitative extraction	Partial extraction	No extraction
1 M HNO_3	Au^{III}, Bi^{III}, Th, U^{VI}, Zr	Hg^{II}, Fe^{III}, Sm, Y, Mo^{VI}	Al, Ca, Cu, Ga, Pb, Mg, Ni, V, Zn
1 M HCl	Au^{III}, Bi^{III}, Th, U^{VI}, Hg^{II}, Mo^{VI}	Zr, Fe^{III}	Al, Ca, Pb, Zn, Ca, Cu, Fe^{II}, Ni, Sm, V, Y

In the extraction of thorium nitrate by tetraalkylmethylenediphosphine dioxides (S) [98] it was established that, in the presence of an excess of the extractant, complexes having the composition $Th(NO_3)_4.2S$ are formed in the organic phase. When there is a deficiency of the extractant, the complexes $Th(NO_3)_4.S$ are present in the organic phase.

Mrochek and Banks[75] quote comparative data for the extraction of praseodymium, neodymium, samarium, and thulium from nitric, hydrochloric, and perchloric acid solutions by tetrahexylalkylenediphosphine dioxides. After assessing the possibility of the employment of diphosphine dioxides as extractants for the separation of the lanthanides, the authors concluded that their selectivity is insufficient for this purpose.

An extensive study of the extraction properties of many tetraalkylmethylenediphosphine dioxides was carried out by O'Laughlin, Banks, and coworkers. Tetra-(n-hexyl)-methylenediphosphine dioxide proved to be extremely convenient as the stationary phase for the extraction chromatography of various metals, including the lanthanides[99]. A study of the extraction of samarium, thorium, and uranium from nitric acid solutions established that tetraalkylmethylenediphosphine dioxides with straight-chain alkyl groups are better extractants than compounds with branched side chains; compounds with branched side chains are relatively more effective for uranium(VI) than for thorium; the partition coefficients of samarium are much lower than those of thorium and uranyl[100].

The significant difference between the separation factors of lanthanide nitrates, chlorides, and perchlorates for separation with the aid of methylenediphosphine dioxides containing straight-chain and branched-chain alkyl groups (hexyl and 2-ethylhexyl) was explained by steric factors[101].

A detailed study of the separation of the lanthanides, thorium, and uranium with the aid of tetra-(n-hexyl)methylenediphosphine dioxide showed that the degree of separation increases appreciably with increase of the concentration of the nitric and hydrochloric acids[102]. Zirconium was isolated and determined in the presence of a large amount of niobium with the aid of the same dioxide used as the stationary phase[103]. In the extraction of the lanthanides from aqueous solutions of hydrochloric, nitric, and perchloric acids by tetraalkylmethylenediphosphine dioxides in carbon tetrachloride or 1,2-dichlorobenzene solution it was found that, tri- or di-solvates are formed, depending on the extractant concentration[104].

Alkylenediphosphine dioxides having the general formula $R_2P(O)-(CH_2)_n-P(O)R_2$, where $R = C_6H_{13}$ and $n = 1$, 4 or 5, have been used to extract tervalent actinides[105]. A study of the distribution of scandium between a nitric acid solution and a solution of tetraoctylethylenediphosphine dioxide in benzene established that the partition coefficient of scandium is directly proportional to the square of the extractant concentration in the organic phase and inversely proportional to the square of the concentration of hydrogen ions in the aqueous phase[106]. The extraction of cerium with the same extractant was also studied[107] and the same relations were established as in the experiments with scandium. In the extraction of radioactive europium(III) from hydrochloric acid solutions by mixtures of 2-thenoyltrifluoroacetone (S) with $(n\text{-}C_6H_{13})_2P(O)-(CH_2)_n-P(O).(C_6H_{13})_2$ (S′) (where $n = 1$, 3, or 4) in cyclohexane adducts having the composition $Eu.S_3.S'$ are formed in the organic cyclohexane phase and synergism is observed[108].

An unusual instance of extraction of the lanthanides by tetraphenylethylenediphosphine dioxide was described recently[109,110]. Praseodymium, europium, and thulium are extracted from the $LiNO_3-KNO_3$ eutectic melt at 160°C. The organic phase is a mixture of biphenyl, *o*-terphenyl, and *m*-terphenyl in which the extractant concentration is 5×10^{-5} M. Two pairs of elements were separated: praseodymium–europium and praseodymium–thulium. In the extraction of americium, curium, and californium under analogous conditions using tetraphenylalkylenediphosphine dioxides $Ph_2P(O)-(CH_2)_n-P(O)Ph_2$, where $n = 2$, 3, or 4, as the extractants lower partition coefficients are observed than for praseodymium, europium, and thulium.

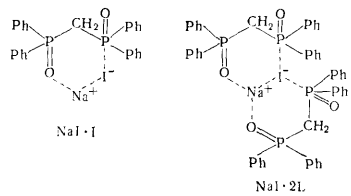
4. COMPLEX-FORMING PROPERTIES

a. Complexes with Alkali Metal Halides

The authors of the present review[111] established that methylenediphosphine dioxides form stable crystalline complexes with alkali metal iodides having the composition $2R_2P(O)CH(R')P(O)R_2.MX$.

Hewerson et al.[112], who oxidised tetraphenylmethylenediphosphine with hydrogen peroxide in acetone in the presence of sodium bromide, isolated the crystalline complex $[(PH_2P(O)CH_2P(O)Ph_2)_3Na]Br.3H_2O$, in which the sodium cation is chelated by three molecules of tetraphenylmethylenediphosphine dioxide with formation of a trigonal prism containing six oxygen atoms.

Yatsimirskii et al.[114] investigated the interaction of alkali metal halides with tetraaryl(alkyl)methylenediphosphine dioxides in non-aqueous solutions. They employed for this purpose conductimetric, spectrophotometric, interferometric, solubility, and other methods. The results obtained in the study of the formation of a sodium iodide complex with tetraphenylmethylenediphosphine dioxide[113] suggested that the entire NaI molecule (ion pair) is involved in the formation of complexes. At this stage of the investigation the hypothesis was put forward that the bond linking the iodide ion to the phosphorus atom can be formed partly as a result of the electrostatic interaction but is mainly due to the overlapping of the orbitals of the ion with the free non-bonding *d* orbitals of phosphorus. The complex formed can be stabilised by the inclusion in its composition of the alkali metal ion. There is then a possibility of the formation of a six-membered ring in which the alkali metal ion interacts electrostatically with the iodide ion and the oxygen atom on which a negative charge is localised. The ring can be built up also on the other side with formation of a condensed complex. The structures of the complexes NaI.L and NaI.2L might have been represented as follows according to this hypothesis:



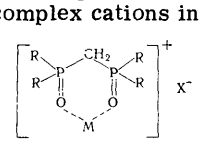
However, further study led to findings conflicting with this hypothesis. Thus, according to ^{31}P NMR data, the two phosphorus atoms are magnetically equivalent, while according to the hypothesis they are non-equivalent. The determination of the real structure of the complexes evidently requires further studies.

To elucidate the influence of the nature of the alkali metal halide on the type of its interaction with phosphine oxides a study has been made of the electrical conductivity of the MX–$Ph_2P(O)CH_2P(O)Ph_2$–acetonitrile system[114], and it has been found that, depending on the nature of the cation and anion in the MX molecule, complex formation can proceed in accordance with one of the following equations:

$$M^+ + X^- + nL \rightleftarrows MX \cdot nL \quad , \qquad (1)$$

$$MX + L \rightleftarrows [ML]^+ + X^- \quad . \qquad (2)$$

The electrically neutral complexes described above arise in the first case and complex cations in the second:



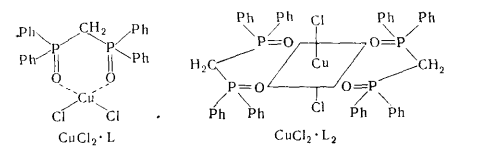
The formation of complexes of the type MX.L or $[ML]^+X^-$ obeys a specific relation: the most favourable conditions for the formation of electrically neutral complexes are created in systems containing a cation with a small radius and a high ionic potential and a large readily polarisable anion. The influence of the structure of phosphine oxides and of the nature of the substituents on the properties of the complexes formed has been studied. A quantitative estimate of the complex-forming properties of phosphine oxides has been made on the basis of the stability constants of their complexes with NaI (the electrically neutral complexes NaI.L) and LiCl {the positively charged complexes $[Li.L]^+$}.[115] The stability of the NaI.L complexes depends significantly on the nature of the substituent at the phosphorus atom. The phenyl group, which can behave both as an electron-donating and an electron-accepting agent, permits the formation of a more stable complex than, for example, the butyl group which behaves as an electron donor only or the butoxy-group which behaves more as an electron acceptor. The complex with an asymmetric dioxide proved to be the most stable.

The interaction of alkali metal halides with tetraalkyl-(aryl)alkylenediphosphine dioxides containing different numbers of methylene groups linking the phosphorus atoms[116], different substituents in the phenyl groups[117], and different substituents in the methylene bridge[118] has also been studied. The results of these investigations are discussed below (see Section 5).

b. Complexes with Copper and Other Metal Salts

The interaction of copper(II) chloride with tetraphenylmethylenediphosphine dioxide $Ph_2P(O)CH_2P(O)Ph_2$ in acetone leads to the formation of the complexes $CuCl_2.L$ and $CuCl_2(Ac)_2$, which can be isolated from solution[119]. At low ligand concentration in solution the product is the complex $[CuCl.L]^+$, while in the presence of an excess of the ligand the complex containing copper(II) chloride and the ligand in the proportions 1 : 2 is formed when the solutions are allowed to stand. The absorption spectrum of the 1 : 1 complex contains a charge-transfer band at 21 000 cm^{-1}; the 1 : 2 (M : L) complex does not exhibit such properties. The stability constant of the complex $[CuCl.L]^+$ was determined from spectrophotometric and conductimetric data.

The structures of the complexes formed can be represented schematically as follows:



In the $CuCl_2.L$ complex all four electron-donating atoms (two O atoms and two Cl atoms) are probably located in the same plane. In the $CuCl_2.2L$ complex the four oxygen atoms are probably located in the equatorial plane (the XV plane) and two chloride ions are above and below this plane.

An X-ray diffraction study of the crystalline copper(II) chloride complex with tetraphenylethylenediphosphine dioxide showed that it exhibits a very marked deviation from the ideal tetragonal symmetry[120]. Complexes of tetraphenylethylenediphosphine dioxide with cobalt halides have also been obtained. All the complexes are paramagnetic.

Certain complexes of organic copper(I) compounds (phenylcopper, tolylcopper, and others) with tetraphenylmethylenediphosphine and tetraphenylethylenediphosphine have likewise been isolated and characterised[121].

The interaction of copper(II) chloride with substituted tetraphenylmethylenediphosphines[117] and also the influence of the length of the chain between the phosphoryl groups on the complex-forming properties of alkylenediphosphine dioxides[116] were studied by Sheka, Yatsimirskii et al. The results of these investigations are discussed below (see Section 5).

In addition to the complexes of the copper salts, a study was also made of the formation of complexes with salts of other metals. The formation of stable 1:1 complexes of tin(IV) chloride and bromide with tetraphenylethylenediphosphine and tetraphenylbutylenediphosphine dioxides has been described[122]. Complexes having the following compositions

$MoOBr_3[Ph_2P(O)CH_2CH_2P(O)Ph_2]$,
$MoO_2Br_2[Ph_2P(O)CH_2CH_2P(O)Ph_2]$,
$MoOCl_3[Ph_2P(O)CH_2CH_2P(O)Ph_2]$,
$MoO_2Cl_2[Ph_2P(O)CH_2CH_2P(O)Ph_2]$,
$WO_2Cl_2[Ph_2P(O)CH_2CH_2P(O)Ph_2]$,
$WO_2Br_2[Ph_2P(O)CH_2CH_2P(O)Ph_2]$

have been synthesised by treating tetraphenylethylenediphosphine dioxide and molybdenum or tungsten hexacarbonyls with halogens, isolated, and characterised[123].

The complexes of tetraphenylmethylenediphosphine dioxide (L) with rhenium(I) carbonyl halides have been obtained and investigated: $Re(CO)_3L$, $Re(CO)_3LBr$, and $Re(CO)_3LCl$.[124] The formation of magnesium and calcium halide complexes with tetraphenylmethylenediphosphine dioxide (L) was established by studying the electrical conductivity of and ion transport in solutions of magnesium and calcium iodides and chlorides in acetonitrile. The complexes $[Mg.L]^{2+}$ and $[MgI.L]^+$ are formed with magnesium iodide, while the existence of the complexes $[Ca.L]^{2+}$ and $[CaCl.L_2]^+$ has been observed[125] for calcium chloride.

A spectrophotometric study of neodymium chloride solutions with tetraphenylmethylenediphosphine dioxide in butyl alcohol established that the complexes $NdCl_3.nL$ (n = 1 or 3) and $NdCl_3.nL_2$ (n = 1, 2, or 3) are formed in steps[126].

5. DEPENDENCE OF THE EXTRACTION AND COMPLEX-FORMING PROPERTIES ON THE STRUCTURE OF THE LIGANDS

Although the number of publications dealing with polydentate organophosphorus complex-forming agents has increased recently, problems such as the relation between the structure and stability of the complexes, the relation between structure and selectivity of ligand action, the relation between the stability constants of the complexes and the capacity for complex formation in heterogeneous media, as well as many other aspects have not been studied.

Certain general problems in the field of polydentate neutral organophosphorus complex-forming agents were investigated by the authors of the present review. It was of interest to discover the influence of the electronic effects of the environment of the active centre of the ligand on complex formation and also the role of steric and structural factors.

a. The Electronic Effects of Substituents

The dependence of the extracting capacity of tetraarylmethylenediphosphine dioxides $(RC_6H_4)_2P(O).CH_2P(O).(C_6H_4R)_2$ containing various substituents in the *meta*- and *para*-positions in the benzene rings (CH_3O, CH_3, Cl, Br, CF_3, etc.) was studied in relation to uranyl nitrate[127]. It was established by the method involving dilution of the extractant that the complexes $UO_2(NO_3)_2.3S$ and $UO_2(NO_3)_2.2S$ exist in the organic phase. The effective extraction constants were calculated for uranyl nitrate ($\overline{K}$) and a correlation between $\lg\overline{K}$ on the one hand and $\Sigma\sigma^{ph}$ and $\Sigma\sigma$ was established for the trisolvates. It was also shown that there is a linear relation between the extracting capacity of the dioxides and the pK defining their basicity. The effective extraction constant varies within wide limits: from 0.8×10^{10} (for the p-MeO substituent) to 70 ± 20 (for the p-CF_3 substituent).

The formation of complexes with copper(II) chloride has also been studied for the same series of substitued dioxides[117]. The stepwise stability constants of the complexes $[CuCl.L]^+$ were determined and a correlation was established between these quantities and the σ constants of the substituents and the basicity (pK_a) of the ligands. The stability constants are higher the weaker the electron-accepting properties of the substituents: $\lg\beta_{ML}$ varies from 3.74 (for p-CF_3) to 4.62 (for p-MeO).

Next the complex-forming properties of tetraphenylmethylenediphosphine dioxides with a substituent in the methylene bridge, $Ph_2P(O)-CHR-P(O)Ph_2$, were investigated. It was found that in the case of uranyl nitrate either the trisolvates or disolvates exist in the organic phase. The effective extraction constants were calculated for the trisolvate complexes and, although they were found to vary for dioxides with different substituents in the bridge, they nevertheless remained within the limits of the same order of magnitude. On the other hand, as shown above, for dioxides with substituents in the phenyl groups these values vary in the range of 4–5 orders of magnitude. The formation of complexes of copper(II) chloride was studied on the basis of stability constants calculated from spectrophotometric data. It was shown that the bridge-substituted tetraphenylmethylenediphosphine dioxides (R = Cl, Br, I, C_6H_5, or $C_6H_5CH_2$), without functional groups in the substituents capable of a donor-acceptor interaction with the metals, form complexes of the same type whose stability is determined mainly by the inductive properties of the substituents. On the other hand, in the presence of substituents containing functional groups [R = CH_2CH_2COOH, $CH_2CH_2P(O)Ph_2$, $CH_2CH_2P(O).(OH)_2$, etc.], which may be involved in complex formation, the compositions structures, and stabilities of the complexes formed are altered.

b. Effect of the Length of the Bridge Between the Phosphorus Atoms

The phosphoryl groups in alkylenediphosphine dioxide molecules are electronegative and exert on one another an influence which weakens the complex-forming capacity of the dioxides. An increase of the distance between the phosphoryl groups reduces their mutual influence. On the other hand, the dimensions and stability of the rings of the chelate compounds formed depend on the number of methylene units in the bridge. Allowance for these factors makes it possible to suggest that the length of the alkylene bridge between the phosphoryl groups can have a significant influence on the complex-forming properties of the dioxides.

Mrochek et al. demonstrated the influence of the alkylene bridge on the composition of the complexes formed in the extraction of uranyl nitrate by tetrahexylalkylenediphosphine dioxides[85]:

$$(C_6H_{13})_2P(O)-(CH_2)_n-P(O)(C_6H_{13})_2,$$

where n = 1, 2, 3, or 4. The dioxide with the methylene bridge exhibits the highest extracting capacity in this series[75]. Laskorin et al.[128] found that the maximum partition coefficient in the extraction of uranium from nitric

and hydrochloric acid solutions by di- and poly-oxides is observed for tetraoctylethylenediphosphine dioxide; a further increase of the length of the bridge between the phosphorus atoms leads to a monotonic decrease of the partition coefficients of uranium.

The influence of the number of methylene units between the phosphoryl groups on the complex-forming[116] and acid–base properties[129] of alkylenediphosphine dioxides containing aryl or alkyl substituents at the phosphorus atoms has been studied. The dioxides of two homologous series were investigated as ligands:

$$Ph_2P(O)-(CH_2)_n-P(O)Ph_2,$$

where $n = 1 - 3$, and

$$Bu_2P(O)-(CH_2)_n-P(O)Bu_2,$$

where $n = 1-6$.

The results of potentiometric titration of the dioxides[129] in nitromethane led to the hypothesis that the protonation of the dioxides with methylene and ethylene bridges proceeds via the formation of rings with an intramolecular hydrogen bond involving both phosphoryl groups. In the presence of a larger number of methylene units the ring probably ruptures and the second phosphoryl group is protonated.

The interaction of the same alkylenediphosphine dioxides with alkali metal halides and copper(II) chloride was studied on the basis of the changes in the electrical conductivities of solutions of the salts following the addition of the ligand[116]. As already mentioned, neutral complexes are formed with alkali metal iodides in acetonitrile, while the chlorides give rise to positively charged complexes. Dioxides with a methylene bridge ($n = 1$) have the most marked complex-forming capacity, the interaction with the salts being reduced in parallel with the increase of the ring size as the number of methylene groups between the phosphorus atoms increases. For tetrabutylalkylenediphosphine dioxides with $n = 4$ or 6, an enhancement of the complex-forming effect is observed, probably owing to the rupture of the chelate ring, and the addition of two MX molecules to the dioxide molecule (both phosphoryl groups act independently). For tetraphenylalkylenediphosphine dioxides, an increase of n leads to a sharp weakening of the complex-forming properties.

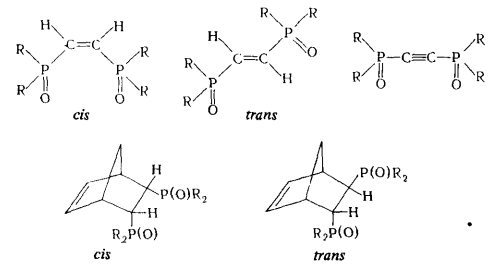
The study of the formation of complexes of copper(II) chloride by spectrophotometric and conductimetric methods showed that tetrabutylmethylenediphosphine and tetrabutylethylenediphosphine dioxides ($n = 1$ or 2) form complexes having the same composition $[CuCl.L]^+$, while for $n = 3$, 4 or 6 ring formation does not occur and the two phosphoryl groups act separately; one cannot rule out the possibility of the formation of polymeric forms of the complexes.

c. Stereochemical Factors

The above data concerning the complex-forming properties of alkylenediphosphine dioxides make it possible in many cases not only to understand but also to predict the nature of the complex formation reaction with particular metals. These considerations apply mainly to the stability of the complexes formed and to the possibility of controlling it largely by varying the electron-donating capacity of the active centre of the ligand.

The problems of the selectivity of the action of the complex-forming agents are a no less interesting and important aspect of the investigation of their properties, since the solution of the problem of selective complex formation is of exceptional significance. However, the principles of creating a complex-forming agent with a high selectivity in relation to the specified metal are still far from being elucidated. Certain studies on these lines were undertaken by the present authors, who began with the hypothesis that the inclusion in the molecule of the complex-forming agent of fragments preventing the free rotation of the individual units and fixing the disposition of the electron-donating atoms would increase the selectivity and efficiency of the complex-forming agent.

This hypothesis was tested by investigating the extraction and complex-forming properties of alkylenediphosphine dioxides with a "rigid" structure, containing a vinylene bridge or a triple bond between the phosphoryl groups: the dioxides of the *cis*- and *trans*-isomers of tetraphenylvinylenediphosphine; tetraphenylethynylenediphosphine dioxide; bicyclic adducts of dioxides containing *cis*- and *trans*-vinylene bridges with cyclopentadiene:



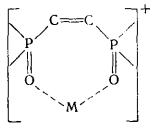
The extraction capacity was studied in relation to nitric acid and uranyl nitrate[130]. It was shown that the partition coefficient of uranyl nitrate is higher by three order of magnitude when the *cis*-isomer of the dioxide with the vinylene bridge is used compared with the dioxide containing an ethylene bridge. Conversely, by fixing the P=O groups in the *trans*-positions, the degree of extraction is reduced to the level characteristic of the corresponding monoxide. The adducts of the *cis*- and *trans*-dioxides with cyclopentadiene behave similarly. The lowest extraction capacity is characteristic of the compound with the ethynylene bridge. The formation of rings is impossible with *trans*-isomers of the dioxide with the ethynylene bridge (the disposition of the atoms in P–C≡C–P is linear). The appreciably enhanced extraction of uranyl nitrate by *cis*-tetraphenylethynylenediphosphine dioxide compared with dioxides containing methylene and ethylene bridges can be attributed to a rigid steric distribution of the phosphorus atoms because, on the one hand, the entropy component of the free energy changes, and, on the other, the distance between the oxygen atom decreases. Possibly it becomes optimal as a result of the formation of rings with uranyl nitrate. Similar results were obtained in a study of the extraction of molybdenum[131].

Thus steric factors have a very significant influence on the extraction properties of the complex-forming agent.

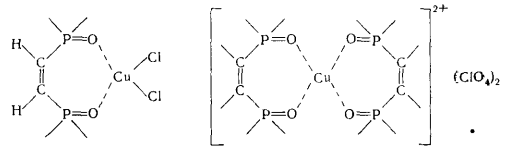
Analogous data were secured in a study of the influence of steric factors on the complex-forming properties of alkylenediphosphine dioxides[132]. The influence of the mutual disposition of the phosphoryl groups in vinylenediphosphine dioxides on the properties of the complexes which they form with certain alkali and transition metal halides was studied. Methylenediphosphine dioxides form electrically neutral cyclic complexes with lithium and sodium iodides as a result of the incorporation in the complex of the ion pair M^+I^-.

The *trans*-isomers of dioxides with a vinylene bridge also form electrically neutral complexes, which shows that the *trans*-disposition of phosphorus atoms apparently makes it possible to form monomeric complexes with the ion pairs M^+I^-.

The interaction of the *cis*-isomer with the same salts results in the formation of positively charged complexes—in this case the cation adds to the oxygen atoms of both phosphoryl groups:

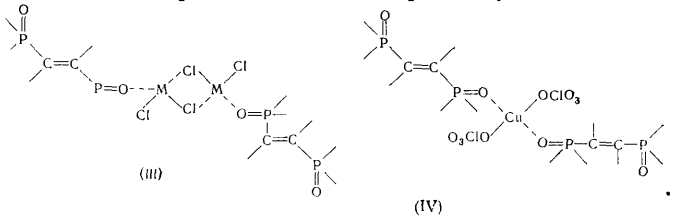


Complexes of the isomeric vinylenediphosphine dioxides have been obtained with cobalt(II) and copper(II) salts. On the basis of reflection and infrared spectroscopic data, structures (I) and (II) were attributed to the crystalline complexes of the *cis*-isomers having the composition $CuLCl_2$ and to the complexes $CuL_2(ClO_4)_2$ respectively:



(I) (II)

Structures (III) and (IV) are most probable for the cobalt(II) and copper(II) complexes with the *trans*-isomers and for the complex $CuL_2(ClO_4)_2$ respectively:



(III) (IV)

Coordination compounds of the dioxides with nickel chloride were obtained by fusing the components at the melting points of the dioxides. The chlorides of the transition metals investigated form 1 : 1 coordination compounds and the perchlorates form 1 : 2 complexes.

The absorption spectra of cobalt complexes show that the absorption band due to the *d*–*d* transition is in the region characteristic of tetrahedral complexes. In the spectra of the copper complexes the band of the *d*–*d* transition is in the near infrared, which suggests that the symmetry of the chromophore in the copper complexes is intermediate between tetrahedral and square planar. At high temperatures the complexes of nickel chloride have spectra characteristic of tetrahedral complexes, while at room temperature the structure of these complexes becomes largely octahedral, which is confirmed both by the spectra and the magnetic moments.

The band due to the vibrations of the free P=O group persists in the infrared spectra of the complexes with the *trans*-isomers of the dioxides and a new band appears, which can be attributed to the vibration of the P=O group bound to the metal. In this case the dioxide behaves as a monodentate ligand, i.e. it combines with the metal via one phosphoryl group. In the spectra of the complexes with the *cis*-isomer the bands due to the vibrations of the P=O group are displaced, which implies that both phosphoryl groups are linked to the metal and the ligand is bidentate.

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