ORGANOPHOSPHORUS COMPLEXONES

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ABSTRACT

The advances of synthetic methods resulted in the development of a series of new and highly effective organophosphorus complexones operating in a broad range of pH values and exhibiting high selectivity. The principal method of producing these substances (polyaminopolyphosphonic acids) is condensation of carbonyl compounds with di- and polyamines and trivalent phosphorus compounds capable of diad tautomerism. The components of this reaction were widely varied, thus yielding a variety of complexones of the general type $([OH]_2P[O]CR_2NCH_2CH_2)_2X$ where X is a heteroatom. The range of synthetic complexones was increased by including complex-forming groups as well as P[III] in the molecules.

The specific behaviour of organophosphorus complexones stems from the peculiar structure and properties of the phosphoryl group $P(O)(OH)_2$: the considerable difference between the first and second ionization stages, the high polarizability of the PO_3 dianion, and the tetrahedral structure of the phosphonate anion, which distinguish organophosphorus complexones from their carbon analogues. Studies of the complex-forming properties of the substances synthesized revealed their specific properties of which the most characteristic are as follows: ability to form di- and polynuclear complexes, including heteronuclear ones, as well as 'hydrogen complexes', preferential formation of strong complexes with multi-charge cations of a small atomic radius (beryllium, iron, germanium); ability to form strong complexes with large radius cations (rare-earth elements, uranium, thorium and zirconium). Alkaline earth metals form rather weak complexes with organophosphorus complexones.

It has been shown that complexone selectivity may be improved by the introduction of 'rigid unit' sites into the molecules.

Complexones are very important substances in the chemistry of coordination compounds. Until recently, they have been mainly used as titrants or masking agents in chemical analysis. The scientific and chemical progress requires, however, new complexones possessing pre-set problem-oriented properties. A set of complexones whose complex-forming ability varies over a wide range is necessary, with emphasis being put on complexones forming complexes maximally stable in a broad pH range and on complexones exhibiting high selectivity.

The first problem may be solved by combination of highly basic nitrogen atoms with polydentate salt-forming groups. The second problem is not solved so easily, as metal ions with close physical and chemical properties, dimensions, steric configurations, and with close ability to complex formation are to be coordinated. The difficulties become even more pronounced when we remember that the polydentate nature and spatial structure of complexones generate a great number of their conformations embracing a range of bond angles and bond lengths, therefore complexones readily respond to geometrical requirements of cations.

A higher selectivity of chelation, particularly with polydentate compounds, may be achieved when the reagent structure is specified as to the total of the properties of the ligand arrangements and the cation, and to the presumed structure of the chelate. Electron densities at the coordination sites and rigidity of the system are very important.

We constructed ligand molecules of pre-set properties by varying dentation, nature of the donor atoms and their closest environment, that is, electron density distribution at the coordination sites, stereochemistry of the molecule of the whole, the number and dimension of the cycles to be closed, the rigidity of the system, etc.

One of the new and promising methods of forecasting complexone structure is the introduction of an iminoalkylphosphonic group as the main complex-forming component of the molecule[1–3].

The specificity of the chelating agent containing the phosphonic group is due to its stereochemistry which is quite different from that of the carboxylic group. The phosphonate ion is nearly tetrahedral (a distorted tetrahedron) with the symmetry axis of third order. The carboxylate ion is planar and has a plane of symmetry. The valence angles and bonds lengths are different.

π-Bonding between the oxygen and phosphorus atoms is considerably weaker than that between the oxygen and carbon atoms in the carboxylic group. Polarizability of P=O bonds in the phosphoryl group is higher than that of C=O bonds in the carboxylic group.

That is why in phosphonic compounds the induction effect plays a role on the one hand, and they have great nucleophilicity of the phosphonic group on the other hand. Due to the stereochemistry of these complexones having two hydroxyls capable of coordination, an *a priori* assumption was that stability of their chelates might be increased by formation of additional cycles and that the complexones should be very selective to cations of increased coordination capacity and of high electrostatic properties.

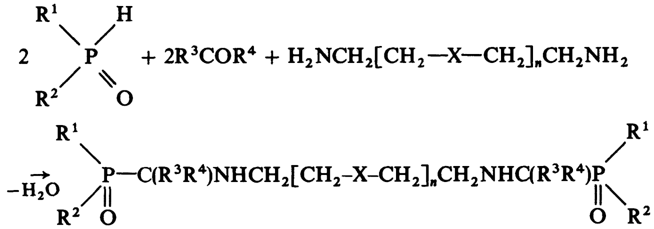
Although the first paper by Schwarzenbach *et al.* on complex-forming properties of aminoalkylenephosphonic acids was published as early as 1949, the most interesting and specific properties of organophosphorus complexones were not described. Nor were they described in later works by Martell, Banks and Yorik who studied the phosphorus derivatives of the widely known complexone ethylenediaminetetraacetic acid (EDTA). Interaction of phosphorus-containing complexones with cations of various groups in D. I. Mendeleev's Periodic Table was thoroughly investigated by using potentiometric, polarographic, i.r., n.m.r. and e.p.r. spectroscopic methods.

At the time we began our studies of polyaminopolyphosphonic acids they were not commercially available. That is why we had to develop some synthetic methods for preparing compounds of that type.

In the early 'fifties we worked out a method to synthesize α-aminoalkylphosphonic acids via the simultaneous or successive action of trivalent phosphorus compounds capable of diad tuatomerism on an amine and an oxo compound. The method is a basis of the present studies.

In the preparation of alkylenediaminodi- and polyphosphonic acids the role of the amine is played by the corresponding diamine (usually ethylenediamine); the role of the oxo compound is played by aldehydes or ketones, or Schiff's bases prepared from the diamine and the oxo compound beforehand.

The phosphorus component may be obtained from any derivative of phosphorous or phosphonic acids. When a two-stage method is used, esters are initial compounds, for example, dialkylphosphites or phosphonites; then the ester group is saponified. In a one-stage method (modification of Moedrizer's method) phosphorous acid is used. For the preparation of ethylenediaminodialkylphosphonous acids we used phosphonous acid.



R^1 = H, OH, OAlk, OAryl, Alk; R^2 = OH, OAlk, OAryl

R^3 = H, Alk, Aryl; R^4 = H, Alk; $n = 0.1$; X = O, NH, S, CH.

On the basis of these methods the following main types of organophosphorus complexones could be prepared:

(1) alkylenepolyaminodialkylaralkyldiphosphonic acids,

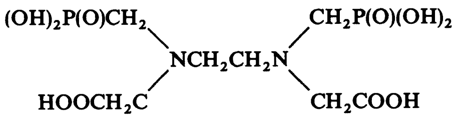
$$(HO)_2P(O)C(R'R'')NHCH_2[CH_2\text{-}X\text{-}CH_2]_nCH_2NHC(R'R'')P(O)(OH)_2$$

R′,R″ = H, Alk, Aryl; $n = 0.1$; X = O, NH, S, CH_2.

(2) alkylenepolyaminopolyalkylphosphonic acids,

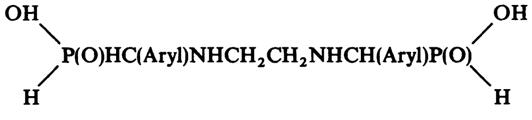
$$[(HO)_2POCH_2]_2NH_2CCH_2N[CH_2PO(OH)_2]_2$$

(3) alkylenepolyaminoalkylphosphonic-diacetic acids,



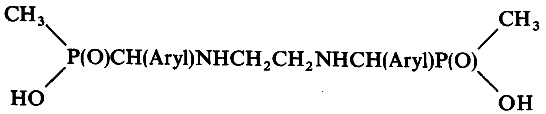
$$\begin{matrix}(OH)_2P(O)CH_2 & & CH_2P(O)(OH)_2\\ & NCH_2CH_2N & \\ HOOCH_2C & & CH_2COOH\end{matrix}$$

(4) alkylenediaminodiarylmethylphosphonous acids,



$$\begin{matrix}OH & & OH\\ & P(O)HC(Aryl)NHCH_2CH_2NHCH(Aryl)P(O) & \\ H & & H\end{matrix}$$

(5) alkylenediaminobisarylmethylphosphinic acids.



$$\begin{matrix}CH_3 \\ HO\end{matrix}\!\!>\!P(O)CH(Aryl)NHCH_2CH_2NHCH(Aryl)P(O)\!<\!\!\begin{matrix}CH_3 \\ OH\end{matrix}$$

So, we have prepared and studied a number of compounds containing phosphonic, phosphonous or phosphinic groups. We have obtained phosphorylated polyamine derivatives, complexones with heteroatoms and aromatic radicals, complexones containing both carboxylic and phosphonic groups, or both hydroxyl and phosphonic groups.

In *Table 1* some of the complexones prepared and their abbreviated names are indicated.

DISSOCIATION OF AMINOPHOSPHONIC ACIDS

Both aminocarboxylic and aminophosphonic acids have zwitterionic structures, similar to that of betaine, but the basicity of the amino group of aminophosphonic acids is higher than that in aminocarboxylic acids (see *Table 2*).

The investigation of deprotonation processes in polyaminopolyphosphonic acids showed that dissociation of a PO_3H_2 group took place at low pH values of the medium. With increasing pH values, PO_3H^- groups dissociate and finally in the alkaline range protons of the betaine nitrogen are split off. When oxyphenyl radicals are present in a complexone molecule, the hydroxyl groups of phenol are the last to dissociate at higher pH values compared with the betaine hydroxyls. In such cases the formation of stable hydrogen bonds is possible.

The comparison of dissociation constants of aminophosphonic and aminocarboxylic acids shows that the last two constants of aminophosphonic acid dissociations, which correspond to betaine proton dissociations, are unusually high and close to each other. The phenomenon is observed more clearly with the diphosphonic acids when the length of the methylene chain between the aminoalkylphosphonic groups increases and the difference between the last dissociation constants decreases by at least an order. This may be assigned to a decrease in the mutual induction effect of the $^+NH_2$ groups.

In the case of tris-, tetra- and pentaphosphonic acids the decrease of mutual influence of the two positive nitrogen atoms may be explained by the high charge of the anion and by electrostatic bonding (hydrogen bond) of the betaine protons with negative oxygen atoms of the phosphonic groups.

As may be seen from *Table 2*, an increase in the number of iminomethylphosphonic groups starts with increasing the last two dissociation constants in going from EDMP to EDTP, but then, in going from EDTP to DTPP the constants do not change further in practice. This is due to an increase of nitrogen basicity corresponding to the higher negative charge of the molecule. When the charge is high enough, the introduction of an additional group changes it rather weakly. A similar phenomenon is observed with phosphates.

Table 1. Complexones and their abbreviations

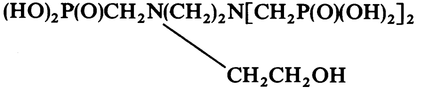
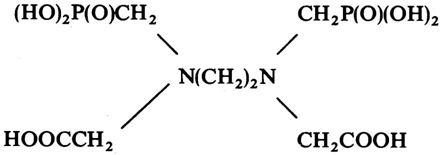
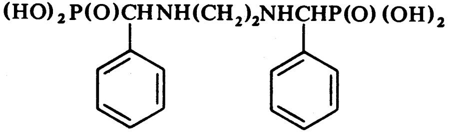
Acid	Formula	Abbreviation
1. Ethylenediaminodimethylphosphonic	$(HO)_2P(O)CH_2NH(CH_2)_2NHCH_2P(O)(OH)_2$	EDMP
2. Ethylenediaminodiisopropylphosphonic	$(HO)_2P(O)C(CH_3)_2NH(CH_2)_2NHC(CH_3)_2P(O)(OH)_2$	EDDIP
3. Oxadiethylenediaminoisopropylphosphonic	$(HO)_2P(O)C(CH_3)_2NH(CH_2)_2O(CH_2)_2NHC(CH_3)_2P(O)(OH)_2$	OAIP
4. Thiadiethylenediamino-*N*,*N*′-diisopropylphosphonic	$[(HO)_2P(O)C(CH_3)_2NH(CH_2)_2]_2S$	TEAIP
5. Diethylenetriamino- *N*,*N*′-diisopropylphosphonic	$[(HO)_2P(O)C(CH_3)_2NH(CH_2)_2]_2NH$	DETAIP
6. Pentamethylenediaminodiisopropylphosphonic	$(HO)_2P(O)C(CH_3)_2NH(CH_2)_5NHC(CH_3)_2P(O)(OH)_2$	PDIP
7. *N*-(2-Hydroxyethyl)ethylenediamino-*N*,*N*′,*N*′-trimethylene-phosphonic	 $(HO)_2P(O)CH_2N(CH_2CH_2OH)(CH_2)_2N[CH_2P(O)(OH)_2]_2$	HEDTP
8. Ethylenediaminotetramethylphosphonic	$[(HO)_2P(O)CH_2]_2N(CH_2)_2N[CH_2P(O)(OH)_2]_2$	EDTP
9. Diethylenetriaminopentamethylphosphonic	$\{[(HO)_2P(O)CH_2]_2N(CH_2)_2\}_2NCH_2P(O)(OH)_2$	DTPP
10. Ethylenediaminodimethylphosphonic-*N*,*N*′-diacetic	 $[(HO)_2P(O)CH_2](HOOCCH_2)N(CH_2)_2N[CH_2P(O)(OH)_2](CH_2COOH)$	EDAP
11. Ethylenediamino-*N*,*N*′-dibenzylphosphonic		EDBPhosphonic

Table 1—continued

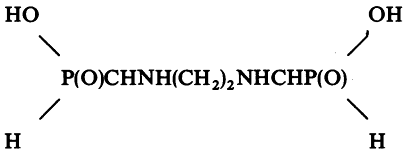
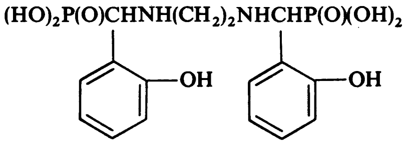
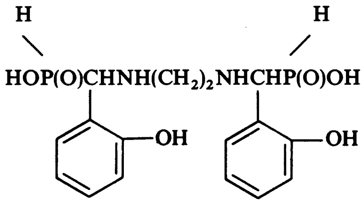
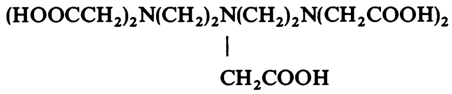
Acid	Formula	Abbreviation
12. Ethylenediamino-*N*,*N'*-dibenzylphosphonous		EDBPhosphonous
13. Ethylenediamino-*N*,*N'*-di-*o*-oxybenzylphosphonic		EDHBPhosphonic
14. Ethylenediamino-*N*,*N'*-di-*o*-hydroxybenzylphosphonous		EDHBPhosphonous
15. Nitrilotrimethylphosphonic	$N[CH_2P(O)(OH)_2]_3$	NTP
16. Ethylenediaminotetraacetic	$(HOOCCH_2)_2N(CH_2)_2N(CH_2COOH)_2$	EDTA
17. Nitrilotriacetic	$N(CH_2COOH)_3$	NTA
18. Diethylenetriaminopentaacetic	 $(HOOCCH_2)_2N(CH_2)_2\underset{\substack{\vert \\ CH_2COOH}}{N}(CH_2)_2N(CH_2COOH)_2$	DTPA

Table 2. pK values of phosphorus-containing compounds

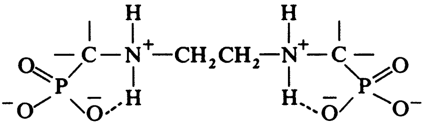
Name	pK_1	pK_2	pK_3	pK_4	pK_5	pK_6	pK_7	pK_8	pK_9	pK_{10}
EDTA	2.0	2.67	6.16	10.26						
EDMP	4.61	5.72	8.02	10.47						
EDDIP	4.81	6.00	8.55	11.24						
OEIP	5.11	6.15	9.80	10.88						
TEAIP	5.51	6.34	10.38	11.48						
DETAIP	5.39	6.55	10.40	11.20						
PDIP	5.77	6.13	11.0	11.0						
HEDTP			3·0	5.23	6.54	8.08	10.18	12.10		
EDTP	1.46	2.72	5.05	6.18	6.63	7.43	9.22	10.60		
DTPP			2.8	4.45	5.50	6.38	7.17	8.15	10.10	12.04
EDAP	1.5	2.30	4.65	6.13	8.36	10.34				
EDBPhosphonic	4.18	5.56	7.44	9.69						
EDBPhosphonous	4.32	7.58								
EDHBPhosphonic	4.37	5.41	6.44	9.95	11.19					
EDHBPhosphonous	4.61	7.54	10.84	11.25						

The introduction of the hydroxyl group into the complexone structure increases deprotonization of the last hydrogen atom.

The combining of highly basic nitrogen atoms and polydentate salt-forming groups in molecules of alkylenepolyaminopolyalkylphosphonic acids allows deprotonation in a wide range of pH values, which enlarges the pH range of the complex stability.

COMPLEXES WITH ALKALI METALS

All organophosphorus complexones form complexes with alkali metals. For example, ethylenediaminodiisopropylphosphonic acid in the range of dissociation of betaine protons, that is at a pH of 8, forms equimolar complexes (log K_{st} LiX 3.06, NaX 2.30, KX < 1, CsX 3.37) of higher stability than those of EDTA. We explain this by the specific action of the phosphonic group and, particularly, by participation of both oxygen atoms of the hydroxyl groups at phosphorus in complex formation. The phosphonic groups of EDDIP begin to participate in the coordination of alkali metals only at rather high pH values, which may be explained by the necessity for hydrogen bond rupture,



resulting in the liberation of all the oxygen atoms of the phosphonic groups, and also by need for increasing the total negative charge of the molecule.

COMPLEXES WITH ALKALINE EARTHS AND WITH BERYLLIUM

Aminopolyalkylenepolyphosphonic acids with not more than two phosphonic groups in practice do not form complexes with alkaline earths including calcium. By increasing the number of the phosphonic groups and also by combining them with carboxylic ones, complexones are prepared which form stable complexes with alkaline earths, the complex stability being of eight to nine orders (see *Table 3*). In these complexes the protonation extent varies with the pH of the medium.

Table 3. Logarithms of stability constants of complexes MX

Cation	Complexones			
	EDDIP	EDAP	EDTP	DTPP
Mg^{2+}	<2	8.54	8.63	6.40
Ca^{2+}	<2	9.02	9.33	7.11

Successive protonation occurring in the usual complexes at decreasing pH values may be demonstrated with magnesium complexes of nitrilomethylphosphonic acid (see *Table 4*).

In the i.r.-spectrum of the $[MgL]^{4-}$ solution the symmetrical νC—H stretching frequency is *ca.* 50 cm^{-1} higher compared with the entirely deprotonated free ligand. This is due to the formation of the stable covalent bond Mg—N. The Mg—N bond formation agrees also with the fact that the p.m.r. proton doublet and the phosphorus triplet are shifted upfield compared with the free ligand.

Table 4. The i.r. and n.m.r.-spectra of magnesium complexes of nitrilotrimethylphosphonic acid

Complex anions	ν CH cm^{-1} AS	S	ν PO_3 cm^{-1}	δ, p.p.m.	δ ^{31}P p.p.m.
MgL^{4-}	2946 2877	2841	1099, 1968 971	3.20	16.63
$MgHL^{3-}$	3000	2937	1106 973	2.83	7.65
MgH_2L^{2-}	2998	2946	1164, 1103 971	2.76	7.20
MgH_3L^-	—	—	1167, 1084 966	—	—
L^{6-}	2939 2845	2790	1083 969	3.45	17.67

The bond between the magnesium atom and the oxygen atoms of the phosphonic groups is mainly ionic which is confirmed by just a slight increase in PO_3 vibration frequencies of the complex compared with the ligand.

On addition of the first proton to the complex the bond N—H is formed with simultaneous 100 cm^{-1} increase of CH stretching frequencies. The second proton is added to the oxygen atom of one of the phosphonic groups, which is reflected by the PO_3H band at 1164 cm^{-1}. The third proton is added to the second phosphonic group (the intensity of the band at 1164 cm^{-1} is increased). All these conclusions agree with n.m.r. ^1H and ^{31}P spectra.

Special attention should be paid to the ability of these compounds to form stable complexes with beryllium (see *Table 5*).

Table 5. Logarithms of stability constants of beryllium complexes

Complexone	BeH_2L	Be_2H_2L
EDMP	8.76	11.4
EDDIP	7.65	11.39
PDIP	6.15	11.21
EDAP	7.15	11.64

The investigation of the complex formation mechanism showed that beryllium atoms interacted only with the phosphonic groups, but the nitrogen atoms of iminoalkylenephosphonic groups did not participate in complex formation. Free coordination sites in the complexes may be occupied by other cations, polynuclear complexes with two coordination sites being formed in this case with two different cations (see *Table 6*).

Table 6. Logarithms of stability constants of polynuclear complexes of ethylenediaminodiisopropropylphosphonic acid

M^{2+}	$BeMH_2L$	$AlMH_2L$	$LaMH_2L$	$CdMH_2L$
Mn	8.7	9.8	6.2	6.9
Fe	8.8	10.0	6.3	7.0
Co	8.9	10.1	6.3	7.0
Ni	8.9	10.3	6.3	7.0
Cu	13.5	14.8	11.4	11.8
Zn	10.1	11.3	7.2	7.8

COMPLEXES WITH TRANSITION ELEMENTS

Specific interaction of organophosphorus complexones with transition elements leads to formation of stable hydrogen complexes, unlike the case of the carboxylic analogues[4]. Copper complexes are the most stable among the normal complexes (see *Table 7*).

Table 7. Logarithms of stability constants of transition metal complexes

No.	Complexone	Cu^{2+}	Ni^{2+}	Co^{2+}	Zn^{2+}	Mn^{2+}	Cd^{2+}
1	NTP	17.75	11.96	14.37	>16.37	10.20	11.55
2	EDDIP	8.83	3.84	3.84	4.81	3.57	
		20.35	11.23	11.19	13.38	8.00	
3	EDTP	11.14	9.12	8.51	9.90	6.99	8.81
		18.95	15.30	15.49	17.05	12.70	13.88
4	EDAP	9.4	9.49			7.0	
		18.5	15.23	16.03	16.85	13.63	

The stability constant of the EDDIP (phosphicin) copper complex is two orders higher than that of EDTA. Very interesting is the great difference between the stabilities of copper complexonates and of other transition metal complexonates. For instance, the stability of the phosphicin copper complex is nine orders higher than those of nickel and zinc complexes (whereas with EDTA the stabilities are of the same order). By e.p.r. and electron spectroscopy methods it was found that in the ground state of the copper(II) complex with ethylenediamino-*N*,*N*′-diisopropylphosphonic acid the unpaired electron occupied the level $d_{x^2-y^2}$ (the axes x and y are directed to the donor atoms of the ligand), so the complex has an elongated octahedron structure. The copper atom is bound to the two nitrogen atoms situated on the plane of the unpaired electron localization, the other coordination sites being occupied by the oxygen atoms of phosphonic groups. The plane bonds of the complex are covalent which is characteristic of copper complexes.

Easily hydrolysable elements such as iron, aluminium, indium, gallium, titanium and chromium form stable complexes with phosphorylated derivatives of polyamines. The particularly high stability of their hydrogen complexes should be mentioned; in a number of cases it is higher than those of the normal complexes of the corresponding aminopolycarboxylic acids.

The interactions may be illustrated by aluminium nitrilotrimethylphosphonate formation.

Aluminium forms two types of complexes with nitrilomethylphosphonic acid: scarcely soluble polynuclear compounds and soluble compounds. In the range of dissociation of the first three protons (at pH from 2.3 to 3.1) the insoluble compound $Al_3H_3L_3 \cdot 9H_2O$ is formed.

With an increase of pH values and at the components ratio AL : NTP = 1 : 1, gradual dissolving of the polynuclear complex takes place with the formation of the soluble monocomplex. AlHL. Further increase of pH values leads to the acidic dissociation of the complex with the formation of the stable normal monocomplex AlL^{3-}.

With excess of aluminium at pH 5–6 a scarcely soluble binuclear complex, Al_2L, is formed and is precipitated in the form of a hexahydrate.

P.m.r. spectroscopy of the normal complex showed the presence of an Al—N bond.

The difference in the chemical shifts with respect to the entirely deprotonized ligand reaches 0.28 p.p.m. The addition of an excess equivalent of alkali (pH 6.86–9.08) does not lead to precipitation, nor to any changes in the n.m.r. spectra. Further addition of the alkali (pH 9.1–10.7) leads to two pairs of bands, the first of which, the intense one, corresponds to the aluminium complex, and the second, the weak one, to the monoprotonized form of the ligand, HL. Further increase of pH values results in higher intensity of the second pair of bands with the subsequent levelling of the bands which is accompanied by precipitation of aluminium hydroxide from the solution.

Probably the complex AlL^{3-} is at equilibrium with the monohydroxocomplex $[(AlOH)HL]^{3-}$ in the solution, which may be explained by high aptitude of aluminium to form bonds with hydroxyls of water. On the other hand, this assumption fits in with the bands in the i.r.-spectrum of the complex, due to formation of an NH bond. Probably the existence of such a 'disproportionated' water molecule in complexes should be characteristic in general of the compounds of easily hydrolysable cations.

The interaction between organophosphorus complexones and iron is of particular interest.

Ethylenediaminobis-(isopropylphosphonic) acid forms with iron(III) a soluble complex which is stable even after the addition of ten equivalents of alkali. Ethylenediaminotetramethylphosphonic acid (EDTP) forms with iron even more stable complexes than does diethylenetriaminopentaacetic acid.

The investigation of i.r., n.m.r. and e.p.r. spectra of iron complexes with carboxylic and phosphorus-containing complexones, as well as potentiometric studies, show that at low pH values the mechanisms of interaction between cation and ligands of these two types are quite different. Carboxylated amines form highly stable water-soluble complexes of the ratio 1:1, whereas phosphorylated amines exist in the presence of Fe^{3+} in the form of protonated polynuclear water-insoluble complexonates of the polymer type. The internal sphere of the complex of phosphorus-containing complexones is due only to the oxygen atoms of the phosphonic groups. In neutral or weakly alkaline media the stability of Fe^{3+} complexes with NTA, EDTA and the like, is substantially decreased due to hydrolytic processes resulting in weakening the bonds between the oxygen atoms of carboxylic groups and the central atom; as to the complexes with phosphorylated ligands, their stability is increased.

The polynuclear complexes are transformed into normal soluble mono- and dinuclear complexes. The complex stabilities are increased due to closure of a thermodynamically favourable cycle with the bonds Me—N; e.p.r. spectra of iron complexonates allowed us to find the environment symmetry of the central atom.

The spectra of the compounds are characteristic of Fe^{3+} in its high spin state σ_A, that is, they have a broad symmetric line indicative of the hexagonal symmetry of the local environments of the iron ion; the splitting due to a tetra- or trigonal component of the crystal field is absent. These data are in good agreement with the results of the determination of magnetic susceptibility of the complexes ($\mu_{eff} = 5.86$, $\rho = s/2$).

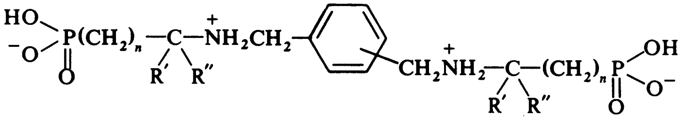
The introduction of hydroxyl into the chelating compounds raises the complex stabilities. *N*-(2-Hydroxyethyl)-ethylenediaminotrimethylphosphonic acid keeps iron from hydrolysis even when refluxing its compounds at a pH of 12.

Ethylenediaminobis-*o*-hydroxybenzylphosphonic and -phosphonous acids form with iron(III) and titanium(IV) superstable highly coloured complexes. The mechanisms of complex formation are, however, quite different: in the case of phosphonous acid, complex formation is possible by simultaneous participation of all donor atoms in coordination, whereas with phosphonic acids, which are characterized by a higher degree of dentation, competition probably takes place between the oxygen atoms of the phosphonic group and the phenoxide ion.

The potential capability of aminoalkylenephosphonic acids to increase dentation due to the oxygen atoms of the phosphonic groups facilitates their complex formation with rare earth elements (REE), which have high coordination numbers and high affinity for oxygen. The stability of hydrogen complexes of phosphicin with REE is close to that of normal complexes of ethylenediaminodiacetic acid, and the stability of hydrogen complexes of EDTP is six to seven orders higher. Certain selectivity to some REEs is observed.

Uranyl ion coordination is of special interest, as the stability of its hydrogen complexes with phosphorylated polyamines is very high. Selectivity of the ligands was improved by increasing the rigidity of the polymethylene chain between iminoalkylenephosphonic groups. As an example xylylenediaminobis-(isopropylphosphonic) acids may be mentioned, which have an aromatic cycle in the chain between the nitrogen atoms; the chain hinders free rotation of the individual units, providing fixed positions of the donor atoms. These acids are quite effective complexing agents only with large cations of REE and with uranyl ions, while they are weak complexing agents in the case of transition metals including iron(III) (see *Table 8*).

Table 8. Logarithms of stability constants of the protonized complexes of xylylenediaminobis-(alkylphosphonic) acids



Position in the nucleus	n	R'	R''	log of $K_{stab.}$ of MH_2X Ni^{2+}	Cu^{2+}	Fe^{3+}	Dy^{3+}	UO_2^{2+}
m-	0	CH_3	CH_3	—	3.92	—	6.48	8.40
p-	0	CH_3	CH_3	—	3	—	4.78	8.32
p-	1	H	H	—	4.08	—	6.17	9.4 precipitate
			EDDIP	3.84	8.83	10	6.20	8.52

Organophosphorus complexones form with most of the elements complicated water-insoluble polynuclear complexes. With nitrylotrimethylphosphonic acid the following equilibria are observed in water solution at pH of 5 to 7:

$$M^{2+} + L^{6-} \rightleftarrows ML^{4-} + 2M^{2+} \rightleftarrows M_3L \rightleftarrows M_3L\downarrow$$

At lower pH values protonized polynuclear complexes of the composition $M_5(HL)_2$ are formed.

The structure of these complexes is hard to be investigated because they are insoluble in water or organic solvents, and amorphous as to an x-ray study. However, i.r.-spectroscopic investigations show that the bond M—N in the compounds is substantially weakened, or absent altogether, and the ring closure occurs via the bonds M—O.

Polyvalent elements forming polynuclear compounds of low solubility have probably coordination number four instead of six, while in solution octahedra are observed. It should be mentioned that the bond between the element and nitrogen is unusually weak in the polynuclear compounds though the coordination with nitrogen is well known. Evidently in this case all the coordination vacancies of the central ion are optimally occupied by the oxygen atoms of the phosphonic groups.

Polynuclear insoluble complexes of the trivalent metals have quite different stabilities in different pH regions. All the complexes of NTP with aluminium and with REE are precipitated in the pH region two or three. The aluminium complex is stable even in 0.1 N hydrochloric acid and so is the ferric complex in 0.2 N HCl where all other complexes are destroyed. The precipitation of a chromium complex is observed only at pH values above three.

All the properties of the polynuclear complexes described above allow one to develop new methods for determining and separating elements with nitrilotrimethylphosphonic acid as analytical reagent (see *Table 9*).

Table 9. Possible determinations of a number of cations in the presence of a number of elements

The element to be determined	Conditions of determination	Elements not interfering with determination	Masking agent
Al	0.1 MHCl	Ni, Co, Cu, Zn, Cd, Mn, Cr, Fe, Ca, Mg, Sr, Ba	DTPA
Fe	2 MHCl	Ca, Mg, Sr, Ba, Be, Al, Ni, Co, Cu, Zn, Cd, Mn	

Aluminium is precipitated as the polynuclear complex $Al_3H_3\text{-}L_2 \cdot 9H_2O$ from an 0.1 N hydrochloric acid solution. Magnesium and alkaline earth metals do not form complexes in these media. Some transition metals such as chromium, copper and zinc form less stable soluble complexes; their obscuring action as well as coprecipitation of transition metals may be easily eliminated by addition of diethylenetriaminopentaacetic acid as masking agent.

Iron complexonate is stable even in a 2 N hydrochloric acid solution; that is why iron can be determined in the presence of the same elements as in the case of aluminium. Very interesting is the possibility of determination of iron in the presence of aluminium, the complex of the latter being destroyed in the medium.

The difficulties of this pair separation, or of the determination of the one element in the presence of the other, are well known.

Our methods may be successfully applied for analysis of polymetallic systems, particularly of various alloys and steels. The investigations in this field are being continued and positive results have been obtained.

The action of phosphorylated polyamines differs from that of the carboxyl analogues, which may be assigned to the internal ligand shell structure that includes a greater number of donor, phosphoryl oxygen, atoms. Stereochemistry of the shell, that forecasts the complex geometry, also plays a role.

We suggest three most probable mechanisms of complex formation of compounds with phosphonic groups. The first mechanism is the formation of the four-membered cycle in which the metal ion is coordinated with two oxygen atoms of the phosphonic group. In this case two modes of metal ion coordination are possible. The first mode consists of metal ion coordination with the two oxygen atoms of the phosphonic group in the middle position: as a result the ligand field attains nearly octahedral or tetrahedral configuration, but the oxygen atoms are not situated at the apices of the corresponding polyhedron and form a new distorted polyhedron with the metal coordination number being higher than usual.

The suggestion does not exclude, however, some possibility of complex formation with four-membered cycles, in which the oxygen atoms of the phosphonic groups are situated at the apices of the polyhedra. Our rough calculations show that the strain of the cycles with oxygen atoms, which are in sp^2-hybridization, is not so high.

The second mechanism suggested is formation of the eight-membered cycle with at least two metal ions being coordinated by the four oxygen atoms of the two phosphonic groups.

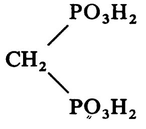
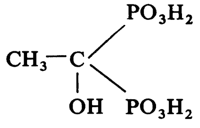
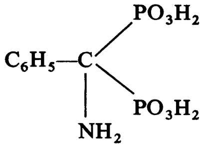
In this case an increase in complex stability is possible due to internal hydrogen bonds formed between the coordination water and the oxygen atoms of the phosphonic groups.

And the third type of coordination is the formation of the crosslinked polymer with the phosphonic group as tridentate site of the ligand. The Stewart molecular models are in good agreement with our suggestions.

HYDROXY- AND AMINOALKYLIDENEBISPHOSPHONIC ACIDS

The conclusion that phosphorylated complexes can form stable hydrogen complexes is based on the assumption that just donor phosphonic oxygen properties work at the interaction with cations. This prompted us to undertake an extensive study of complex-forming agents containing two phosphonic groups attached to a carbon atom. As we expected, these alkylidenediphosphonic derivatives have been found to interact with cations in acidic media, up to 6 N nitric acid (see *Table 10*)[2].

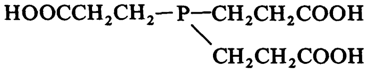
Table 10. Logarithms of stability constants of complexes of alkylidenediphosphonic acids

								
	ML	ML_2	ML	ML_2	M_2L	ML	ML_2	M_2L
Be^{2+}	8	19.1	16.5		25.7	26.2		23.4
Al^{3+}	14.1	23.0	15.3	25.9	27.2	18.8	26.3	23.1
Fe^{3+}	19.9	26.6	21.6		29.2	20.2	27.5	
Ln^{3+}	12–13	20–22	18–20		15–16	16–17	22–24	

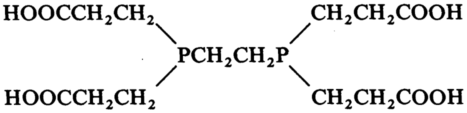
These compounds are quite promising due to their selective action towards beryllium, aluminium, titanium and thorium, and due to their availability.

COMPLEXONES WITH THREE-VALENT PHOSPHORUS

Specificity of complex formation by organophosphorus complexones has allowed us to solve a number of interesting problems. However, polyamine derivatives are not fit to coordinate some elements, such as silver, mercury, vanadium and molybdenum, in aqueous media. We consider that complexones in which trivalent phosphorus atoms replace nitrogen donor atoms may be quite useful in solving the problem.



$HOOCCH_2CH_2{-}P(CH_2CH_2COOH)_2$



$(HOOCCH_2CH_2)_2PCH_2CH_2P(CH_2CH_2COOH)_2$

These metals form stronger bonds with trivalent phosphorus atoms because, besides with the metal–phosphorus σ-bond, a $d\pi$-bond is formed through electron transition of the $4d$ lone pair to the closely lying phosphorus d-orbital. Hence, stable complexes are formed just with these elements.

We are now investigating phosphine derivatives which combine in their molecules donor atoms of a trivalent phosphorus group and acid phosphonic groups. This is a new type of promising ligands.

Unique properties of organophosphorus complexones give the possibilities of their applications in various branches of science and technology. They are effective metal detoxicants, in cleaning heat and power equipment, in dissolving corrosion deposits, in separating neighbouring elements, particularly rare earth elements[1].

In chemical analysis the new specific complexones have been used for selective determinations, which are hardly fulfilled with EDTA.

Progress in the chemistry of organophosphorus complexones makes us expect further development of theoretical and practical investigations of these compounds.

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