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Abstract

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ON CERTAIN FEATURES OF COMPLEX FORMATION BY ORGANOPHOSPHORUS COMPLEXONES

One of the important tasks of coordination chemistry is the creation of selective multidentate reagents. In this respect, phosphorylated derivatives of polyamines are interesting complex-forming compounds, combining increased denticity, distinctive stereochemistry, and a certain specificity of action of the phosphine grouping.

The data available in the literature on the synthesis of organophosphorus complexones and the study of their complex-forming properties are few and do not permit conclusions to be drawn about the specificity of the action of the phosphine grouping introduced into the chelant system (1–9).

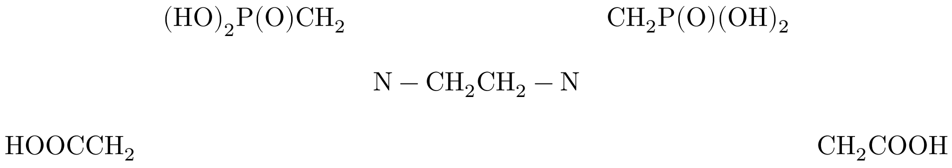
In the present work, the complex-forming ability of ethylenediaminebismethylphosphonic (I), ethylenediaminebisisopropylphosphinic (II), and ethylenediaminebismethylphosphonic-bisuccinic (III) acids (3,4) was investigated.

$$(HO)_2P(O)CH_2-NHCH_2CH_2NH-CH_2P(O)(OH)_2$$

(I)

$$(HO)_2P(O)C(CH_3)_2-NHCH_2CH_2NH-C(CH_3)_2P(O)(OH)_2$$

(II)

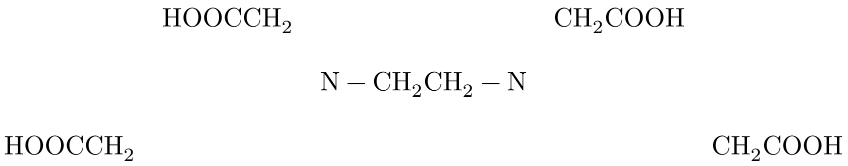


$$\begin{array}{ccc} (HO)_2P(O)CH_2 & & CH_2P(O)(OH)_2 \\ & N-CH_2CH_2-N & \\ HOOCCH_2 & & CH_2COOH \end{array}$$

(III)

$HOOCCH_2-NH-CH_2CH_2-NH-CH_2COOH$

(IV)



$$\begin{array}{ccc} HOOCCH_2 & & CH_2COOH \\ & N-CH_2CH_2-N & \\ HOOCCH_2 & & CH_2COOH \end{array}$$

(V)

The constants of acid dissociation of the complexones themselves, the composition of the complexes, the optimal conditions for their formation, and shifts of half-wave potentials during complex formation over a broad range of pH values, taking kinetics into account, were determined. The instability constants of the complex compounds were determined by two parallel methods—potentiometric and polarographic (12–14).

Some of the results obtained are presented in the graphs (Figs. 1, 2, 3) and collected in the table, where, for comparison, data are also given for the carboxyl-containing analogues IV (9,10) and V (11).

As is seen from the potentiometric titration curves (Figs. 1, 2, curve 1) and the dissociation constants (Table 1), compounds I and II are tetrabasic acids, while III is a hexabasic acid, with structures of a double betaine. The course of the potentiometric titration curves in the system

Table 1

Logarithms of the stability constants of complexes with certain metals

Compound	Logarithm of the acid dissociation constants	Mg	Ca	Sr	Cu	Ni	Co	Zn	Mn	Fe^{3+}	Be	Y	La	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tu	Yb	Lu
I	$pK_1 = 4.61$				8.72	4.71	3.84		3.63			8.79		7.98	8.31	8.43	8.54	8.31		8.79					
I	$pK_3 = 8.02$																								
I	$pK_4 = 5.72$	<2	<2	<1	18.52	12.02	10.80		7.55	>10	>7											>			
I	$pK_2 = 10.4$				8.83	3.84	3.84	4.81	3.57	>10		6.48	5.37		5.82	6.20		6.16		6.40		6.88			7.67
II	$pK_1 = 4.95$																								
II	$pK_3 = 8.55$																								
II	$pK_2 = 6.00$																								
II	$pK_4 = 11.68$	<2	<2	<1	20.35	14.13	11.19	13.38	8.00		7	12.87	10.13		11.60	12.56		12.27		12.89		13.39			13.37
III	$pK_1 = 4.3$											9.2	8.43			9.6						9.2			9.2
III	$pK_4 = 6.1$																								
III	$pK_2 = 2.30$				9.49	9.49										17.8						17.7			17.7

Compound	Logarithm of the acid dissociation constant	Mg	Ca	Sr	Cu	Ni	Co	Zn	Mn	Fe^{3+}	Be	Y	La	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tu	Yb	Lu
III	$pK_5 = 8.36$																								
III	$pK_3 = 4.65$																								
IV	$pK_6 = 10.34$	8.11	7.91	6.89	18.5	15.23				>12															
IV	$pK_2 = 6.22$	3.9			16.2	13.5	11.2					7.78	7.04	7.84	8.06	8.28	8.38	8.13	8.18	8.31	8.42	8.59		8.93	9.09
IV	$pK_1 = 9.46$																								
V	$pK_1 = 2.00$																								
V	$pK_3 = 6.16$	8.69	10.59	8.63	18.80	18.62	12.31	16.51	14.04	25.1		18.05	15.56	16.46	16.61	17.14	17.35	17.37	17.93	18.30		18.85	19.32	19.51	19.83
V	$pK_2 = 2.67$																								
V	$pK_4 = 10.26$																								

of the complexone–metal (Fig. 1, 2, curves 2-7) indicates that the nature of the interaction does not change on passing from ethylenediaminebis(methylphosphinic acid) (I) to ethylenediamine-N,N′-dimethylphosphinic-N,N′-diacetic acid (III). For the cations studied (see Table 1), except for the alkaline-earth cations, at an equimolar ratio of the components in the initial

Figure 1: Potentiometric titration curves

Figure 1: Figure 1: Potentiometric titration curves

Figure 2: Potentiometric titration curves

Figure 2: Figure 2: Potentiometric titration curves

mixture there is observed the formation of hydrogen complexes, accompanied by the dissociation of all the hydrogens of the complexone except the two betaine hydrogens. It should be noted that these compounds are highly stable in comparison with carboxyl-containing analogs. In the pH region of dissociation of the betaine protons, normal complexes are formed. The potentiometric titration curves (Fig. 1, 2) have two clearly expressed buffer regions, corresponding to the formation of hydrogen and normal complexes. For such cations as iron, chromium, aluminum, manganese, thorium, and the REE, the formation of hydroxo complexes is also characteristic. In the case of cations capable of exhibiting coordination number eight (REE, Th), the formation, in excess reagent, of acid complexes of composition $Me(H_2X)_2$ was noted (Fig. 1, curves 6, 7).

Attention is drawn to the distinctive behavior of complexone II with respect to

···of iron; forming a soluble complex compound in the pH region of dissociation of the betaine proton (Fig. 1, curve 5), iron does not pre-

Fig. 1. Curves of potentiometric titration (25°, 0.1 M KCl).
1 –ethylenediamine N,N′-diisopropylphosphonic acid (I) $1 \cdot 10^{-3}\ M$;
2 –(II) $1 \cdot 10^{-3}\ M + NiCl_2\ 1 \cdot 10^{-3}\ M$;
3 –(II) $1 \cdot 10^{-3}\ M + YCl_3\ 1 \cdot 10^{-3}\ M$;
4 –(II) $1 \cdot 10^{-3}\ M + CuCl_2\ 1 \cdot 10^{-3}\ M$;
5 –(II) $1 \cdot 10^{-3}\ M + FeCl_3\ 1 \cdot 10^{-3}\ M$;
6 –(II) $1 \cdot 10^{-3}\ M + LaCl_3\ 1 \cdot 10^{-3}\ M$;
7 –(II) $1 \cdot 10^{-3}\ M + LaCl_3\ 5 \cdot 10^{-4}\ M$.

Fig. 2. Curves of potentiometric titration (25°, 0.1 M KCl).
1 –ethylenediamine N,N′-dimethylphosphonic-N,N'-diacetic acid (III) $1 \cdot 10^{-3}\ M$;
2 –(III) $1 \cdot 10^{-3}\ M + MgCl_2\ 3 \cdot 10^{-3}\ M$;
3 –(III) $1 \cdot 10^{-3}\ M + NiCl_2\ 1 \cdot 10^{-3}\ M$;
4 –(III) $1 \cdot 10^{-3}\ M + LaCl_3\ 1 \cdot 10^{-3}\ M$;
5 –(III) $1 \cdot 10^{-3}\ M + CuCl_2\ 1 \cdot 10^{-3}\ M$.

cipitates even in the presence of 10 equivalents of alkali. In this case the solution changes color from light yellow to wine-red, gradually passing into the colloidal state and then into a gel. This, probably, can be explained by the formation in solution of a polycyclic chelate compound of polymeric type. In this compound, apparently, hydroxyl ions serve as the corresponding cross-link; this is indicated

Figure 3: Polarograms of cobalt reduction

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by the gently sloping form of the titration curve, which shows that even after the addition of four equivalents of alkali further binding of hydroxyl ions takes place.

Fig. 3. Polarograms of cobalt reduction:
1 $-1 \cdot 10^{-4}$ M Co^{2+} + pH 9.35;
2 $-1 \cdot 10^{-4}$ M $\mathrm{Co}^{2+} + 1 \cdot 10^{-4}$ M II;
3 $-1 \cdot 10^{-4}$ M $\mathrm{Co}^{2+} + 1 \cdot 10^{-3}$ M beryllium complexonate with II.

Also of considerable interest is the capacity of compounds I and II for complex formation with beryllium (Table 1). By the high-frequency and complexmetric titration with beryllon as indicator, the existence of several complexes I and II with Be of composition Be : Me from 1 : 2 to 1 : 6 was established. The strength of the latter chelate exceeds the strength of the corresponding compound of beryllon with Be, whose pK is equal to 7. In this respect the organophosphorus complexones differ substantially from ordinary complexones and many other chelates, the large volume of whose coordinating groups hinders interaction with cations of small volume.

In polarographic and potentiometric investigation of complex beryllium-complexonate—metal ion systems, the fact of formation of bimetallic heterocyclic complexes

$$\mathrm{BeY} + \mathrm{Me} \rightleftharpoons \mathrm{BeYMe}$$

was established (Fig. 3). As is seen from the polarographic curves, the cobalt reduction wave decreases upon addition of the complexone owing to formation of the complexonate (CoY) (curve 2); upon addition of beryllium complexonate an even greater decrease is observed (curve 3)—owing to formation of a bimetallic complex whose strength exceeds the stability of ordinary complexes.

Comparison of literature and our data on the study of phosphorylated derivatives of polyamines and their carboxyl-containing analogs (Table 1) makes it possible to draw certain conclusions about the specificity of the behavior of organophosphorus complexones. Although in these complexones, as in the carboxyl-containing analogs, cyclization can occur through metal—nitrogen and metal—oxygen bonds, a definite difference is observed in their behavior.

For organophosphorus complexones, a high strength of hydrogen complexes is characteristic, as is a different sequence of change in the strength of metal complexes, and a much greater difference in instability constants between the corresponding copper and iron complexonates and the complexonates of other metals.

An explanation of this may be sought in the specificity of the behavior of the phosphine grouping, which in certain cases is potentially capable of exhibiting additional denticity, and in the stereochemical features of the $-PO_3$-group.

The realization of cyclization by closure in the chelate of four- and five-membered rings with formation of low-strain structures of high strength is a new property of complexones with phosphine groupings. It is probably precisely this property that explains the comparatively large difference in the instability constants of the hydrogen and normal complexes of ethylenediaminedisuccinic acid and ethylenediaminebis(methylenephosphonic) and bis(isopropylphosphonic) acids.

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