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POLYNUCLEAR BERYLLIUM COMPLEXONATES

This communication is devoted to a study of the formation of polynuclear beryllium complexes with complexones whose molecules contain alkylphosphinic groupings. We have studied the following complexones:

1) ethylenediaminebismethylphosphinic acid
$H_2O_3PCH_2NHCH_2CH_2 \cdot NHCH_2PO_3H_2$ (I);

2) ethylenediaminebisisopropylphosphinic acid
$H_2O_3PC(CH_3)_2 \cdot NHCH_2CH_2NHC(CH_3)_2PO_3H_2$ (II);

3) oxabisethylenaminoisopropylphosphinic acid
$(H_2O_3PC(CH_3)_2 \cdot NHCH_2CH_2)_2O$ (III);

4) thiabissethylenaminoisopropylphosphinic acid
$(H_2O_3PC(CH_3)_2 \cdot NHCH_2CH_2)_2S$ (IV).

In a small number of works (1) it has been shown that similar complexones form mononuclear complexes with various metals, and nothing is said about the possibility of formation of beryllium complexonates.

The investigation was carried out by the methods of potentiometric titration (on an LP-58 potentiometer with a glass electrode; reference electrode–SCE; measurement accuracy ±0.02 pH) and polarography (on LP-55 and 7-77-4/v polarographs). All experiments were carried out in a nitrogen atmosphere at 25±0.01°C. The constant ionic strength of the solution ($\mu = 0.1$) was maintained with KCl. Reagents of chemically pure grade were used.

As an example, complex formation with complexone (III) is considered.

Figure 1 shows the titration curves: (1) for free complexone (III) (10^{-3} mole/liter) and for mixtures of Be^{2+} : complexone (III) in the ratios: 2—1 : 1, 3—2 : 1, 4—3 : 1, as well as the titration curve of Be^{2+} (10^{-3} mole/liter) with alkali (5). Curve 1 has two buffer regions at $a = 0$–2 and $a = 2$–4; the first corresponds to titration of two acid protons, the second to two betaine protons. On curve 4 the region $a = 3$–5 is analogous to curve 5 ($a = 0$–2). On curve 3 there is also a small buffer region at pH 6.3, corresponding to the region

Fig. 1 and Fig. 2 diagrams

Figure 1: Fig. 1 and Fig. 2 diagrams

$a = 1–2$ on curve 5, where the process of precipitation of $Be(OH)_2$ occurs. This leads to the conclusion that a complex containing more than one beryllium ion per phosphinic grouping is not formed. On curves 2 ($a = 3–4$) and 3 ($a = 4–6$) at pH 8.3 there is a buffer region; the number of hydroxyls in it is equal to the number of beryllium ions entering the complex. In this region a precipitate of $Be(OH)_2$ begins to separate from the solution. Thus, in the indicated buffer region a second hydroxyl, required for precipitation of the hydroxide, is added to the beryllium ion; i.e., the first hydroxyl is added to the beryllium complexonate immediately before this buffer region, and the region of its addition, by analogy with curve 5 ($a = 0–1$), is extended, which is explained by oxolation processes (2). The region $a = 0–2$, therefore, corresponds to titration of two protons displaced by Be^{2+} from the complexone. From all that has been said above it follows that the formation of the beryllium complexonate, the formation of the beryllium hydroxo complex, and its subsequent destruction do not affect,

apparently, the betaine protons of the complexon, i.e., Be—N bonds, are not formed.

Thus, in diberyllium complexes of the type $\mathrm{Be_2H_2Y(OH)_2}$ or $\mathrm{Be_2H_2Y(H_2O)_2}$, for two beryllium atoms there are two $-\mathrm{PO_3^{2-}}$ groups and one more addend each ($-\mathrm{OH}$ or $\mathrm{H_2O}$). Since, for steric reasons, a beryllium atom with tetrahedral or square hybridization cannot coordinate with more than one oxygen atom of a single $-\mathrm{PO_3^{2-}}$ group, one must assume coordination of each Be atom with

Fig. 1. Curves of potentiometric titration:
1 $-1 \cdot 10^{-3}$ mol/l of complexon (III);
2 $-1 \cdot 10^{-3}$ mol/l (III) + $1 \cdot 10^{-3}$ mol/l $\mathrm{Be^{2+}}$;
3 $-1 \cdot 10^{-3}$ mol/l (III) + $2 \cdot 10^{-3}$ mol/l $\mathrm{Be^{2+}}$;
4 $-1 \cdot 10^{-3}$ mol/l (III) + $3 \cdot 10^{-3}$ mol/l $\mathrm{Be^{2+}}$;
5 $-1 \cdot 10^{-3}$ mol/l $\mathrm{Be^{2+}}$.

Fig. 2. Scheme of the structure of the beryllium—complexon complex (II): $\mathrm{Be_2H_2Y(H_2O)_2}$

two oxygen atoms of two $-\mathrm{PO_3^{2+}}$ groups. In this case the question of the fourth addend remains open.

It is not possible to construct a model of the diberyllium complex with a beryllium coordination number equal to four without violating the "natural" valence angles; either Be—Be coordination must be assumed, in which case, with a tetrahedral configuration, each Be atom forms a trigonal prism of 6 oxygen atoms around two Be atoms ("P^6 hybridization" of the pseudoatom $\mathrm{Be_2}$), and the molecule is built without strain (upper drawing in Fig. 2); or the formation of a

Fig. 3 and Fig. 4

Figure 2: Fig. 3 and Fig. 4

square from two Be atoms and two O atoms must be assumed, which eliminates the assumption of an unusual Be—Be bond but leads to a strong distortion of the valence angles (lower drawing in Fig. 2).

The question of the structure of these complexes and their geometry, naturally, requires special investigation.

The stability constants of the complexonates were calculated using the Bjerrum method (3,4).

Thus, in solution there may form dinuclear homonuclear complexes Be_2H_2Y (12.46)[*], $Be_2H_2Y(OH)$ (21.45), $Be_2H_2Y(OH)_2$ (29.07), and intermediate monocomplexes BeH_2Y (7.34), $BeH_2Y(OH)$ (15.48).

In the titration of systems (Fig. 3) complexon (III) ($1 \cdot 10^{-3}$ mol/l), Be^{2+} ($1 \cdot 10^{-3}$ and $2 \cdot 10^{-3}$ mol/l), and Ni^{2+} ($1 \cdot 10^{-3}$ mol/l), the Ni^{2+} ion was brought

As an example, the titration curves are analogous to those for the systems Be^{2+}: complexone (III) $= 1 : 1$ and $2 : 1$ at $a = 0$–5 and $a = 0$–6, respectively, but are located at lower pH values than the latter. The buffer region for the addition of the last two hydroxyls may be regarded as the region of hydrolysis of beryllium from the polynuclear heteronuclear complex, since here a precipitate of $Be(OH)_2$ is formed. In addition, there is no enlargement of the buffer region at pH 6.3 (Figs. 2, 4), i.e., Be^{2+} is not displaced from the complex (cf. Fig. 1, 3) by the second metal. Metal ions of the first transition period, selected as the second cation, give complexes of composition 1 : 1 (MY).

Fig. 3. Curves of potentiometric titration:
1 —$1 \cdot 10^{-3}$ mol/l complexone (III);
2 —$1 \cdot 10^{-3}$ mol/l (III) + $1 \cdot 10^{-3}$ mol/l Ni^{2+};
3 —$1 \cdot 10^{-3}$ mol/l (III) + $1 \cdot 10^{-3}$ mol/l Ni^{2+} + $1 \cdot 10^{-3}$ mol/l Be^{2+};
4 —$1 \cdot 10^{-3}$ mol/l (III) + $1 \cdot 10^{-3}$ ml Ni^{2+} + $2 \cdot 10^{-3}$ mol/l Be^{2+}.

Fig. 4. Reduction polarograms:
1, 1a —$1 \cdot 10^{-4}$ mol/l Ni^{2+} (pH 2.5 and 4.4);
2, 2a —$1 \cdot 10^{-4}$ mol/l Ni^{2+} + $1 \cdot 10^{-3}$ mol/l complexone (III);
3, 3a —$1 \cdot 10^{-4}$ mol/mol Ni^{2+} + $1 \cdot 10^{-3}$ mol/l Be^{2+} + $1 \cdot 10^{-3}$ mol/l complexone (III).

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[*] The values in parentheses are the total stability constants of the complexes; they are referred to monomeric compounds; in the case of formation of di-, tri-, or polymeric complexes, the calculated values of the constants, naturally, change.

Table 1 gives the dependence of the logarithms of the concentration stability constants MY and the dependence of the pH of hydrolysis of beryllium from the polynuclear heteronuclear complex on the ordinal number of the ion of the second metal entering the complex. The clear correlation of the results shows that the polynuclear heteronuclear complex is formed.

Table 1

lg K_{MY} and pH of Be hydrolysis

Complex	M^{2+}	lg $K_{\mathrm{MY}} \pm 0.10$	pH
Be^{2+}		–	6.3
$BeH_2Y(OH)_2$		–	8.3
$BeMY(OH)_2$	Ca	5.1	8.2–8.3
$BeMY(OH)_2$	Mn	10.19	8.1–8.2
$BeMY(OH)_2$	Fe	10.90	7.9–8.1
$BeMY(OH)_2$	Co	11.44	7.7–7.9
$BeMY(OH)_2$	Ni	13.13	7.5–7.7
$BeMY(OH)_2$	Cu	18.33	6.4–6.6
$BeMY(OH)_2$	Zn	13.11	7.4–7.6

A polarographic study of the system Be^{2+}:Ni^{2+}:complexone (III) (Fig. 4) shows that the reduction wave of Ni^{2+} (10^{-4} mol/l) at pH 2.5 and 4.4 with an excess amount of complexone (III) (10^{-3} mol/l) in solution (curves 2 and 2a) practically does not change in comparison with the wav-

of free nickel (curves 1 and 1a). Upon addition of Be^{2+} (10^{-3} mol/l) to the system (curves 3 and 3a), the reduction wave of Ni^{2+} shifts sharply in the negative direction and becomes immeasurable.

Analogous phenomena occur in other systems involving divalent metals of the transition period: Be^{2+} : complexon (I)–(IV) over the entire range of pH values (below the hydrolysis of the complex according to Table 1). Thus, all the polarographic investigations confirm the conclusions of the potentiometric studies concerning the formation of polynuclear heteronuclear complexes in the acidic pH region. On the basis of these investigations it may be concluded that the polynuclear heteronuclear complexes have the compositions Be_2MY, $Be_2MY(OH)$, $Be_2MY(OH)_2$, BeMY, and BeMY(OH). The stability constants of these complexes are 2-3 orders of magnitude higher than the stability constants of MY (Table 1). A detailed description of these complexes will be given in a separate article.

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