## LETTERS TO THE EDITOR

## Synthesis, Acid—Base Properties, and Complexing Properties of *N*,*N*-Bis[butoxy(hydroxy)phosphinoylmethyl]glycine

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**Abstract**—*N*,*N*-Bis(dibutoxyphosphinoylmethyl)glycine was synthesized by the Kabachnik–Fields reaction in the three-component system glycine hydrochloride–formaldehyde–dibutyl hydrogen phosphite. Saponification of the product gave *N*,*N*-bis[butoxy(hydroxy)phosphinoylmethyl]glycine as the normal potassium salt. pH-Metric titration was used to determine the ionization constants of *N*,*N*-bis[butoxy(hydroxy)phosphinoylmethyl]glycine, as well as the stability constants of its Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) complexes.

**Keywords:** organophosphorus complexing agents, stability constants of complexes

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Previously we synthesized an organophosphorus analog of the well-known complexing agent nitrilotriacetic acid [1], specifically, potassium salt of aminotris(*O*-butyl methylphosphonic acid), and studied its acid—base and complexing properties with respect to divalent ions of certain transition metals [2, 3]. It was found that this triphosphorylated amine much differs in complexing properties from nitrilotriacetic acid, forming less stable complexes.

Herein, we proposed a method of synthesis of compound 2, a diphosphorylated analog of nitrilotriacetic acid, which, as judged from its structure, should rank between the triphosphorylated amine and nitrilotriacetic acid in complexing power.

Potassium salt of *N,N*-bis[butoxy(hydroxy)phosphinoylmethyl]glycine **2** was prepared by saponification of diphosphorylated amine **1**, which, in its turn, was obtained by the Kabachnik–Fields reaction in the

three-component system glycine hydrochloride–formal-dehyde–dibutyl hydrogen phosphate (Scheme 1).

The ionization constants of N,N-bis[butoxy-(hydroxy)phosphinoylmethyl]glycine (H<sub>3</sub>L) in aqueous solution were determined by pH-metric titration: p $K_1$  < 1, p $K_2$  1.39±0.06, p $K_3$  2.15±0.04, p $K_4$  7.30±0.04.

It was found that salt **2** forms water-soluble complexes with Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) ions. The stability constants (log  $\beta$ ) of 1 : 1 ML<sup>-</sup>, specifically, 6.24, 7.58, 8.21, 9.77, and 8.19 for the Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) complexes, respectively, were determined by potentiometric titration. The resulting stability series agrees well with the Irving–Williams series [4]. The stability constants for compound **2** are higher than the respective values for the triphosphorylated analog by 2.5–3 log  $\beta$  units [2] but are lower of the stability constants of the complexes of nitrilotriacetic acid with the same series

Scheme 1. 
$$H_{3}\overset{\uparrow}{\text{Cl}} \overset{\circ}{\text{OH}} \overset{2(\text{BuO})_{2}P(\text{O})\text{H},}{\overset{2H_{2}C=\text{O}}{-2H_{2}\text{O}}} \overset{\text{BuO}}{\text{BuO}} \overset{\parallel}{\text{P}} \overset{\circ}{\text{N}} \overset{\circ}{\text{OBu}} \overset{3\text{KOH}}{\overset{-H_{2}\text{O}}{-2\text{BuOH}}} \overset{\text{BuO}}{\overset{-H_{2}\text{O}}{-2\text{BuOH}}} \overset{\parallel}{\text{N}} \overset{\circ}{\text{O}} \overset{\circ}{\text{N}} \overset{\circ}{\text{N}} \overset{\circ}{\text{O}} \overset{\circ}{\text{N}} \overset{\circ}{\text{O}} \overset{\circ}{\text{N}} \overset{\circ}{\text{O}} \overset{\circ}{\text{N}} \overset{\circ}{\text{N}} \overset{\circ}{\text{O}} \overset{\circ}{\text{N}} \overset{\circ}{\text{O}} \overset{\circ}{\text{N}} \overset{\circ}{\text{N}} \overset{\circ}{\text{O}} \overset{\circ}{\text{N}} \overset{\circ}{\text{N}} \overset{\circ}{\text{O}} \overset{\circ}{\text{N}} \overset{\circ}{\text{O}} \overset{\circ}{\text{N}} \overset{\circ}{\text{N}} \overset{\circ}{\text{O}} \overset{\circ}{\text{N}} \overset{\circ}{\text{N}} \overset{\circ}{\text{O}} \overset{\circ}{\text{N}} \overset{\circ}{$$