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Dedicated to the 110th anniversary of M.I. Kabachnik's birth

Complexing Properties of Organophosphorus Analogs of Nitrilotriacetic Acid: Aminotris(*O*-alkyl methylenephosphonic Acids)

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Abstract—A series of tribasic aminotris(*O*-alkyl methylenephosphonic acids), the closest organophosphorus analogs of nitrilotriacetic acid, a widely known complexone, were synthesized. The acid–base properties of the synthesized acids were studied, and the stability constants of their 1 : 1 complexes with two-charged cations of alkaline-earth and transition metals were determined.

Keywords: organophosphorus complexones, acid–base properties, stability constants of complexes

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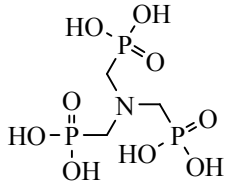
The chemistry of complexones originates from the middle of 20th century, when Schwarzenbach [1] described unique complex-forming properties of aminopolycarboxylic acids: nitrilotriacetic (**1**) and ethylenediaminetetraacetic acids (**2**), demonstrated their use in analytical chemistry, and introduced the term "complexone."

The progress in this field over the later few decades was to a great extent due to the research of Russian scientists M.I. Kabachnik, T.F. Medved', and N.M. Dyatlova, who developed methods of synthesis and studied the complex-forming properties and practical potential of organophosphorus complexones—aminopolymethylenephosphonic acids [2–7]. In this connection, of special mentioning is the pioneering work of Kabachnik and Medved' [8], where they developed a method of synthesis of aminophosphonic acids, which is widely used for the synthesis of organophosphorus complexones and predetermined as a matter of fact all subsequent strategy of the design of aminophosphoryl complexones.

At present the complex-forming properties of nitrilotriacetic and ethylenediaminetetraacetic acids and their organophosphorus analogs nitrilotri(methylenephosphonic acid) (**3**) and ethylenediaminetetra(methylenephosphonic acid) (**4**) have been thoroughly studied and systematized [9].



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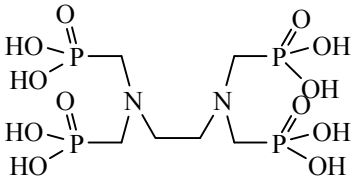

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Even though these acids are formally structurally similar and have the same donor atoms, dentacity in 1 : 1 complexes, and similar coordination entities in the complexes they form, aminopolymethylenephosphonic complexones are quite different from aminopolycarboxylic acids in terms of the stoichiometry of complex-forming reactions in aqueous solutions, having different numbers of proton-donor groups in their molecules. For example, nitrilotriacetic and ethylenediaminetetraacetic acids are tri- and tetrabasic acids, whereas nitrilotri(methylenephosphonic) and ethylenediaminetetra(methylenephosphonic acid) are hexa- and octabasic acids, respectively.

In this connection we considered it interesting to study new-type complexones, which contain a monobasic organophosphorus, for example, *O*-alkyl methylenephosphono group. Stoichiometrically, such