

Review

# Coordination chemistry of polyamines and their interactions in ternary systems including metal ions, nucleosides and nucleotides

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## Abstract

Metal ions and polyvalent organic cations take part in many processes proceeding in living organisms. These processes are associated with the formation of coordination compounds and molecular complexes. An important group of bioligands is made up of biogenic amines, which occur in practically all forms of organisms and their reactions with nucleic acids play an essential role in processes of genetic information transfer. Metals present in cells should be considered as interfering agents, which change the character of interactions. Reactions, including the formation of molecular complexes and metallation of a number of polyamines, have been described. The effectiveness of non-covalent interactions of amines, besides charge, is determined by structural factors (this fact elucidates reaction specificity) and these interactions are of an ion–ion, ion–dipole type, both in binary and ternary systems, that include fragments of nucleic acids (nucleosides, nucleotides) and metal ions, as well. Differences in the character of the interactions can elucidate different biological activity of biogenic amines compared to their analogues, not occurring in living organisms.

Principal metallation sites of discussed bioligands in ternary systems, including fragments of nucleic acids, are amino groups of polyamines and endocyclic nitrogen atoms N(1), N(7) and N(3) of purine and pyrimidine rings of nucleosides as well as phosphate groups of nucleotides, respectively.

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## 1. Introduction

Biogenic amines: putrescine (Put), spermidine (Spd) and spermine (Spm), belong to the group of aliphatic polyamines (PA) (Fig. 1) and take part in many processes proceeding in living organisms [1–3]. A minor role is played by their structural homologues, concentrations of which in the cells are, however, considerably lower.

The bioligand content in living organisms depends on the nature of tissues and cell age [4–11]. An increased PA level was found in young cells as well as in cancer cells [5,12–20] and this observation is useful for clinical diagnostics and treatment process monitoring [21]. The earliest observation in this subject was the effect of polyamines on biological membranes [22–28]. The high level of polyamines in young cells suggests direct interactions between PA and nucleic acids in proliferation processes [29,30]. Taking into consideration the fact that concentrations of polyamines in cancer cells are higher than those in normal ones, the anti-proliferative agents [31,32] were tested for their capability of retarding the development of cancer cells. The strategy of searching for anti-cancer drugs, consisting in PA depletion, still raises hopes, particularly when using anti-metabolites together with other chemotherapeutic agents [21,31]. The presence of polyamines in living cells is associated with changes in DNA and RNA structures at several organisational levels, which determines their role in processes of genetic information transfer. The high basicity of biogenic amines causes that in physiological conditions they occur as protonated species and in such a form they react with fragments of other biomolecules, e.g. with negative (deprotonated) phosphate groups of nucleotides and endocyclic nitrogen atoms of high electron density of purine and pyrimidine bases [33–37]. Manning polyelectrolyte theory suggests that changes in the structure of molecules depend on reactant charge [38,39]. However, such an approach cannot explain the high specificity of some reactions. In addition to electrostatic interactions, structural factors should also be taken into consideration in order to shed light on the nature of the processes [29,40–52]. Although the interactions between PA and nucleic acids and their effect on

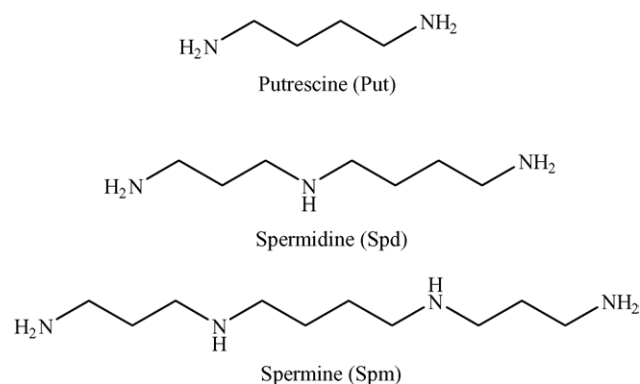


Fig. 1. Biogenic amines.

proliferation and differentiation of cells are unquestionable, the mode and specificity of these interactions, that change the DNA structure, still raise doubts [53].

While analysing these interactions, we cannot neglect the presence of metal ions in living cells. Coordination sites, both in polyamines and nucleosides as well as nucleotides are, at the same time, potential centers of non-covalent interactions. Metal ions, occurring in living organisms, change the character of processes between bioligands and can be considered as interfering agents, competing with polyamine in the reaction with nucleic acid fragments as has been schematically presented in Fig. 2 (single arrows indicate main potential coordination sites and centers of non-covalent interactions).

Many questions concerning the role of metals in living organisms are still far from solved. Their explanation, first of all, needs full recognition of the character of metal–polyamines as well as polyamine–nucleotide interactions in model binary systems, preceding investigation of ternary systems. The results of these observations should yield better insight into intracellular molecular mechanisms of reactions related to metal ions, polyamines and fragments of nucleic acids.

The aim of this work is presentation of current knowledge of such problems as metallation of polyamines, formation of adducts in systems including polyamines and nucleosides or nucleotides, and interactions in ternary

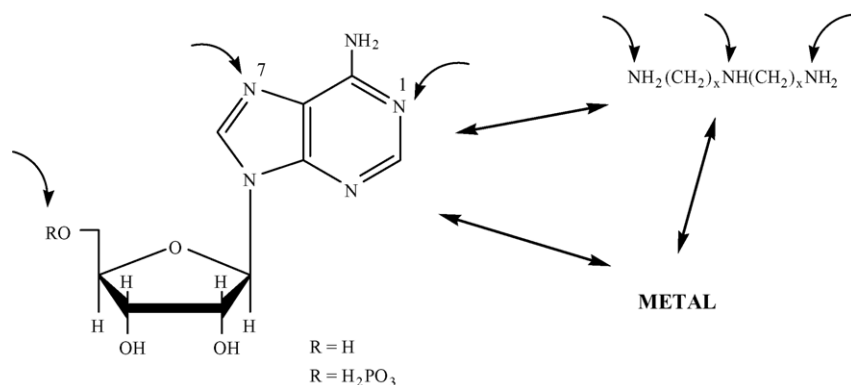


Fig. 2. Scheme of interactions in Nuc(NucP)-PA-metal ternary systems (simple arrows indicate potential donor atoms).

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