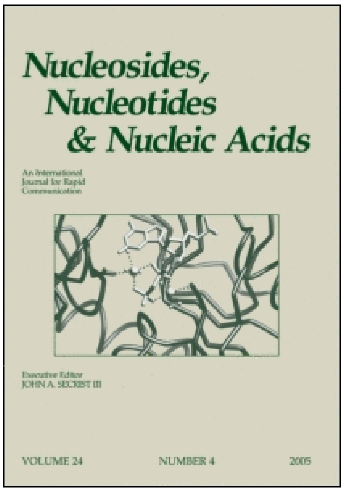

## Nucleosides, Nucleotides and Nucleic Acids

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# Interaction 3d-and 4d-Group Metal Ions With GMP

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# INTERACTION 3d- AND 4d-GROUP METAL IONS WITH GMP

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**ABSTRACT:** The interaction of 3d- and 4d- group metal ions with GMP is studied by the differential UV spectroscopy method. $Ni^{2+}$, $Co^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Cd^{2+}$ form a chelate structure, interacting innerspherically with N7 and outerspherically with O6, while $Ag^{+}$ binds innerspherically to N7 as well as to O6. The difference in association constants for 3d ions binding to GMP is mainly due to differences in the ion radii.

The aim of this work is to establish binding sites and association constants of $Ni^{2+}$, $Co^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Cd^{2+}$ and $Ag^{+}$ ions interacting with GMP in aqueous solution. Note that the main information about the sites of $Co^{2+}$, $Ni^{2+}$, $Zn^{2+}$ binding to GMP and Guo was obtained in DMSO solutions or crystals[1], i.e. systems with suppressed activity of water. The data on $Me^{2+}$-GMP association constants are not numerous and they were obtained on solutions of one ionic strength (I = 0.1 M) by potentiometric titration[2].

Materials and methods: GMP (concentration~$10^{-4}$M), was dissolved in acetate buffer ($10^{-3}$M $Na^{+}$, pH 6.0). The DUV spectra ($\Delta A(\nu)$) were measured using a four-cuvette recording arrangement.

It is seen in Fig 1 that the $Me^{2+}$- and protonation-induced DUV spectra of GMP considerably differ in intensity but they all have similar shapes. The positions of the long wavelength maximum and the isobestic point (i.p.) are approximately identical for all $Me^{2+}$ complexes and agree with what is observed on N7 protonation. This suggests direct binding of $Cu^{2+}$, $Ni^{2+}$, $Zn^{2+}$ and $Co^{2+}$ ions to N7 GMP. The $Ag^{+}$ -induced UVD spectra of

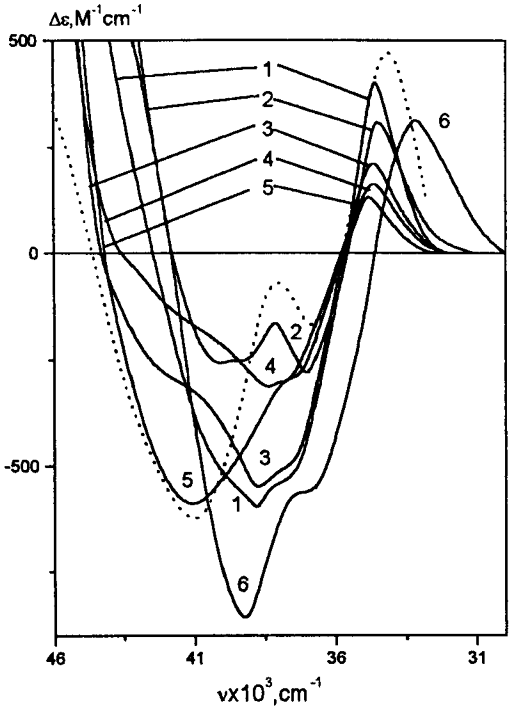

**FIG 1** Differential UV spectra induced by:
1 - $Co^{2+}$ ( $3.5\times10^{-3}$M), 2 - $Cu^{2+}$ ($3\times10^{-4}$M), 3 - $Zn^{2+}$ ($4\times10^{-3}$M), 4 - $Ni^{2+}$ ($4.5\times10^{-3}$M), 5 - $Cd^{2+}$ ($7.5\times10^{-4}$M), 6 - $Ag^{+}$ ($3\times10^{-5}$M)
.......- DUV spectrum due to N7 GMP protonation (its intensity is six times reduced).

**TABLE 1** Association constants of $Me^{2+}$ and $Ag^{+}$ interacting with GMP

| Ion | Ni | Co | Zn | Cu | Cd | Ag |
|---|---|---|---|---|---|---|
| K*0.01,$M^{-1}$ | 35±5 | 14±2 | 15±2 | 150±10 | 40±10 | 130±10 |
| R, A | 0.78 | 0.82 | 0.83 | 0.70 | 1.03 | 1.13 |

R-crystallographic radius of ion

GMP are appreciably different. They display red shift of the long-wavelength maximum and the i.p. against their positions in the UVD spectra induced by protonation of N7 GMP (Fig. 1) and the $Me^{2+}$ ions. It is likely that these features are due to $Ag^{+}$-induced deprotonation of N1. The red shift of the short-wavelength .i.p. in the DUV spectra of metal complexes may be due to the outerspheric ions-O6 interaction inducing the keto-enol transition of guanine. According to quantum mechanical calculation, the keto-enol transition in Guo causes a more considerable bathochromic shift of band III than N7 protonation does[3]. It is important that keto-enol transition may be responsible for the ions-induced transition Guanine + metal ion → Adenine[4].

Binding constants (K) of ions under investigation interacting with GMP are summarized in table 1. The association constants for 3d-ions meat Irwing-Williams sequence[5]. The differences of K-values for 3d ions are caused by different ion radii and, as a result, different surface charge. The differences in $Ag^+$ and $Cd^{2+}$ binding constants is likely due to the different structure of complexes formed by these ions.

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