Conformational change in DNA, as demonstrated for the B → Z conversion leads to the biologically important consequence that the ability of the DNA to act as a template for RNA synthesis is affected. Figure 1 illustrates the correlation of the B → Z transition of poly(dGdC)•poly(dGdC) which occurs at ~60 μM $Co(NH_3)_6{}^{3+}$, with a decrease in RNA synthesis to ~1/2 the original rate, in the presence of *E. coli* RNA polymerase. A decrease in RNA synthesis also accompanies the conversion of a similar double helix in which the guanines are methylated, poly(dGdm^{5}C)•poly(dGdm^{5}C), from the B to the Z form, even though this transition occurs at a much lower (~3 *μM*) Co(III) concentration. Clearly the metal complex has profound effects on the DNA conformation, and the DNA conformation affects the ability of the DNA to act as a template for RNA synthesis.

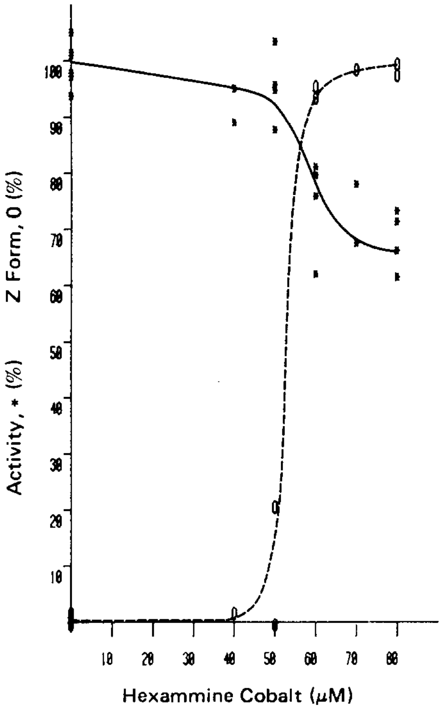

Fig. 1. Correlation between conformational transition (- - -) of poly(dGdC)•poly(dGdC) and change in activity to act as template in RNA synthesis (——).

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T6

A Spectrophotometric Study of tRNA-Cu(II) Complex

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The spectrum of the aqueous copper(II) ion is changed in the presence of the tRNA molecule: a marked increase in absorption and a shift in its maximum from 800 to 740 nm is observed (Fig. 1). This effect is similar to the one observed on coordination of Cu(II) with ammonia and ethylene diamine [1] and is due to the stronger ligand field of the nitrogen derivatives. Therefore our data seem to indicate that the copper hydrated ion exchanges a water molecule with a heterocyclic base of tRNA at one of its nitrogen donor sites creating a coordination complex. The ΔA_{710} value obtained from the differential spectrum (2) in Fig. 1 is proportional to the bound copper concentration. We observed that ΔA_{710} increased immediately as Cu(II) ions were added and the process shows a saturation only for a $[Cu^{2+}]/[PO_4^-]$ ratio greater than 0.5 (Fig. 2). An increase in the NaCl concentration from 0.1 to 0.7 *M* has some influence, however small, on the formation of

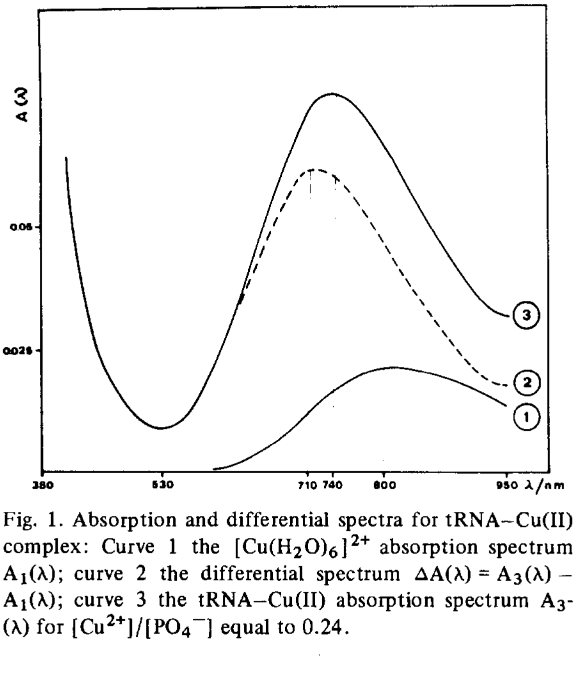

Fig. 1. Absorption and differential spectra for tRNA–Cu(II) complex: Curve 1 the $[Cu(H_2O)_6]^{2+}$ absorption spectrum $A_1(\lambda)$; curve 2 the differential spectrum $\Delta A(\lambda) = A_3(\lambda) - A_1(\lambda)$; curve 3 the tRNA–Cu(II) absorption spectrum $A_3(\lambda)$ for $[Cu^{2+}]/[PO_4^-]$ equal to 0.24.

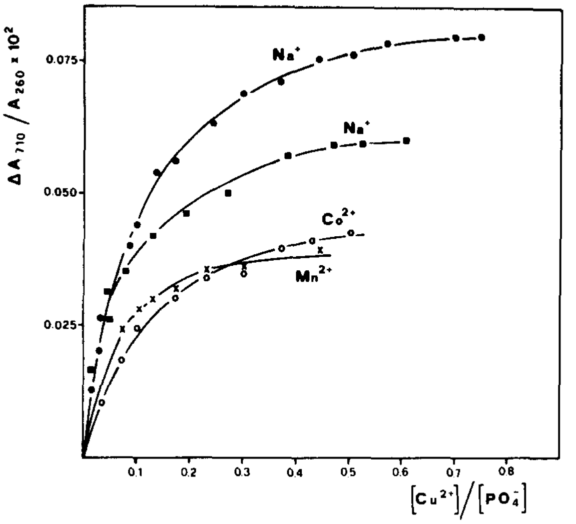

Fig. 2. Experimental curves for the ΔA_{710} dependence on the ratio $[Cu^{2+}]/PO_4^-]$, in the presence of other metal ions: (●) for $[Na^+] = 0.1$ *M*; (▪) for $[Na^+] = 0.7$ *M*; (X) for $[Mn^{2+}] = 0.01$ *M*; (o) for $[Co^{2+}] = 0.01$ *M*. The ΔA_{710} parameter was normalized with respect to A_{260}.

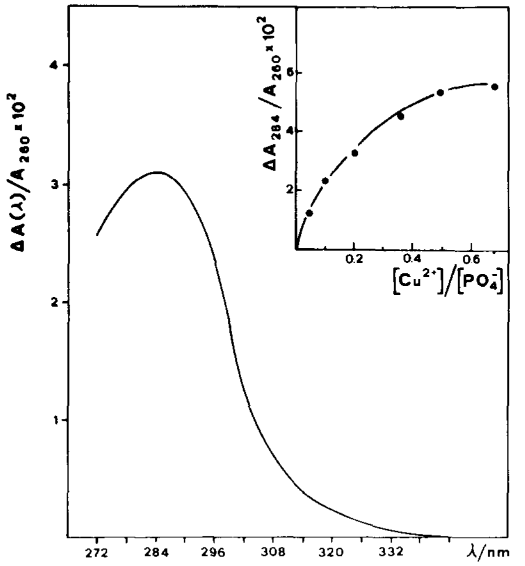

Fig. 3. UV absorption differential spectrum for the tRNA–Cu(II) complex. $[Cu^{2+}]/[PO_4^-] = 0.24$, pH 6. The insert on the top of the figure represents the ΔA_{284} normalized variation with the $[Cu^{2+}]/[PO_4^-]$ ratio.

the tRNA–Cu(II) complex. This influence is manifest mostly at values of the $[Cu^{2+}]/[PO_4^-]$ ratio greater than 0.1. The formation of the copper complex with tRNA is on the contrary hindered by the presence of small quantities of Co^{2+} or Mn^{2+} and this fact suggests competition of the Cu^{2+} ions with the other transition metals for the same sites of the tRNA molecule. A further indication of the transition metal binding to the tRNA heterocyclic bases may be obtained from the analysis of the changes in optical properties of bases which accompany the binding of Cu^{2+}, Mn^{2+} and Co^{2+} ions [2]. When Cu^{2+} is added to the tRNA solution a change in the tRNA electronic spectrum is observed with the appearance of an absorption band in the 280–300 nm range (Fig. 3). A comparison of the absorption changes which follow the varying of the copper concentration at 280 nm (see insert on the top of Fig. 3) with the analogue measure previously performed at 710 nm (Fig. 2) confirmed that both absorption changes were completed in the same copper concentration range, that is they are measurements of the same effect.

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T7

Spectroscopic Investigations of the Binding of Transition Metal Ions to Adenosine-5′-triphosphate

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Adenosine-5′-triphosphate is one of the most important molecules in biological systems, being involved in such divergent functions as mechanical motion, light production, and synthesis of organic compounds. Divalent metal ions are necessary for the biological activity of adenosine-5′-triphosphate, *e.g.* when ATP is present in a biological system as an energy transfer agent, it is most often associated with Mg^{2+} or Ca^{2+}. Thus the interaction of the divalent transition metal ions with ATP is of considerable interest in the search to understand the molecular level of the biological interactions involving ATP [1].

We have examined the spectroscopic properties of the following complexes:

$Na_2\{PdATP\}\cdot 3H_2O$	$Na_2\{ZnATP\}\cdot 3H_2O$
$Na_2\{Cd_3(ATP)_2\}\cdot 4H_2O$	$Na_2\{NiATP\}\cdot 4H_2O$
$Na_2\{HgATP\}\cdot 3H_2O$	$Na_2\{CoATP\}\cdot 2H_2O$
$Na\{UO_2ATPH\}\cdot 4H_2O$	

These complexes were prepared by mixing equimolar aqueous solutions [2] of adenosine-5′-triphosphate with the corresponding transition metal chloride or nitrate salt and then raising the pH to 7 by using a