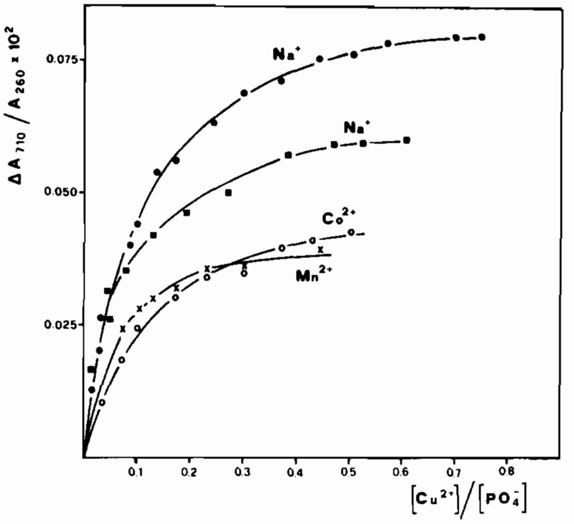

Fig. 2. Experimental curves for the ΔA_{710} dependence on the ratio $[Cu^{2+}]/PO_4^-]$, in the presence of other metal ions: (●) for $[Na^+] = 0.1$ *M*; (▪) for $[Na^+] = 0.7$ *M*; (X) for $[Mn^{2+}] = 0.01$ *M*; (o) for $[Co^{2+}] = 0.01$ *M*. The ΔA_{710} parameter was normalized with respect to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

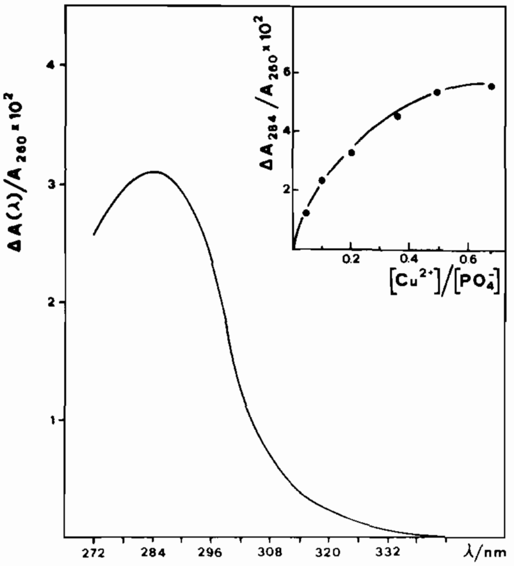

Fig. 3. UV absorption differential spectrum for the tRNA–Cu(II) complex. $[Cu^{2+}]/[PO_4^-] = 0.24$, pH 6. The insert on the top of the figure represents the ΔA_{284} normalized variation with the $[Cu^{2+}]/[PO_4^-]$ ratio.

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 sodium hydroxide solution. The complexes were separated on addition of alcohol under constant stirring. The molar conductance values of the complexes showed that all of them exhibit electrolytic behavior in water and are in accordance with 2:1 electrolytes. The complex $Na\{UO_2ATPH\}\cdot 4H_2O$ was insoluble in water and all other common organic solvents. In the pure $Na_2H_2ATP\cdot 3H_2O$ the band around 1720 cm^{-1} is attributed to the protonated form of the adenine moiety.

This band, however, is strongly pH dependent and shifts to 1650 cm^{-1} in ATP^{4-} attributable to the non protonated form of the adenine moiety [3]. In all complexes prepared except $Na\{UO_2ATPH\}\cdot 4H_2O$ the infrared spectra in that region showed a strong band around 1650 cm^{-1} indicating that the adenine moiety of ATP is in its nonprotonated form. In these cases there is probably coordination of the metal ion through the N-7 of the purine ring. The ^1H and ^{13}C NMR spectra of the complexes with diamagnetic metal ions also verify these results [4]. The presence of a strong band around 980 cm^{-1} along with changes in intensity and/or frequency in the region between 1300–900 cm^{-1} where the P–O vibrations occur [5], establish that except for the mercury complex, in all other complexes the metal ions coordinate also through the phosphate group of adenosine-5′-triphosphate.

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T8

Multinuclear NMR Studies on $ZnCl_2$–, $CdCl_2$– and $HgCl_2$–Interactions with Adenosin and Guanosin and Other Nitrogen-Heterocycles

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^{13}C NMR investigations of nitrogen heterocycles have been established as a useful tool for the detection of protonation sites [1]. The ^{13}C, ^1H spin–spin interactions are particularly sensitive parameters for this purpose, as was shown recently for purine [2]. Even more direct information is available from ^{15}N NMR studies, where chemical shifts are strongly affected by protonation [3, 4].

An extension of such studies to interactions between metal salts and nitrogen heterocycles seemed of interest. The present communication deals with results of ^{13}C, ^{15}N, ^{199}Hg, and ^{113}Cd NMR investigations of adenosin and guanosin in the presence of $ZnCl_2$, $CdCl_2$, and $HgCl_2$ in DMSO-d_6. The information extracted from the various NMR parameters, in particular, ^{13}C,^1H spin–spin coupling constants and ^{15}N as well as ^{199}Hg, and ^{113}Cd chemical shifts is compared, and the contact sites as well as the strength of the interactions are discussed. Similar studies with imidazole and 1-methyl imidazole as well as with purine and its methyl derivatives are described.

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T9

Properties and Structure of Pt(II) Complexes with Adenine and Guanine

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The electroneutral *cis*-dichloro complexes of Pt(II) with DNA purine bases are potential chemotherapeutic agents. Therefore, it was necessary to study their properties and structure. In solving the problem one can also elucidate the effect of the metal ions, introduced into a living body, on the biological action of nucleic acids and their monomeric units. Metal complexes with guanine (Gu) are of special interest as a Gu base is the most reactive fragment of DNA with which both chemical cancer agents and Pt(II) antitumour drugs interact selectively.

The physico-chemical properties and structure of the electroneutral complexes of Pt(II) with adenine (Ad) and Gu obtained by mixing aqueous-acidic solutions of the ligands and the metal salt, K_2PtCl_4, (1:1 mole ratio) were studied. Complexes of the type $PtCl_2L(H_2O)_n$ were synthesized, where L = Ad or Gu, n = 0, 1, 2, 3. The complexes with n = 3 dissolve in DMFA and DMSO and the solutions obtained are practically nonconductors of current and are storage stable. The UV spectra (DMSO) are characterized by the intraligand bands of a charge transfer for $PtCl_2Ad(H_2O)_3$ (I) $\nu = 273$ nm, $\epsilon = 10000$ l mol^{-1} cm^{-1},