compounds have provided a substantial knowledge about modes of interaction between metal ions and phosphoryl groups [1–3]. However, there are only few solid-state studies [4, 5] of metal complexes with adenosine triphosphate (ATP) in spite of the importance of this nucleotide polyphosphate for many biochemical reactions.

In a previous note we reported the syntheses of a series of ternary complexes between ATP, dipyridylamine (DPA) and the metal ions Mg(II), Mn(II), Co(II), Cu(II) and Zn(II) [6]. Subsequently we prepared ternary complexes with the ions Ca(II), Sr(II), Ba(II), Fe(II), Ni(II), Cd(II) and Pb(II).

In order to provide further information about coordination geometry of the metal–ATP system, the X-ray structure analysis of the ternary complexes Mg(II)–ATP–DPA (1), Ca(II)–ATP–DPA (2), Mn(II)–ATP–DPA (3) and Co(II)–ATP–DPA (4) has been performed. The compounds were crystallized from solutions containing a mixture of the appropriate components in the molar ratio 1:1:1. All four compounds crystallize in the orthorhombic space group $C222_1$ (Table I).

TABLE I. Some Significant Crystal Data for the M(II)(ATP)-(DPA) Complexes.

	Mg	Ca	Mn	Co
a (Å)	10.233(3)	10.154(3)	10.234(3)	10.218(3)
b (Å)	22.734(3)	22.965(3)	22.699(3)	22.717(3)
c (Å)	30.997(4)	32.390(4)	31.351(4)	31.027(4)
V (Å^3)	7,211.05	7,552.91	7,282.89	7,202.06
Z	8	8	8	8
Diffractometer	Philips PW1100 (MoK_α)	Philips PW1100 (MoK_α)	Cad-4 (MoK_α)	Cad-4 (MoK_α)
No. of observed reflections ($F > 3\sigma(F)$)	1050	1200	3534	1850

Some attempts to solve the structures of the compounds (1) and (2) by direct methods, using MULTAN 80 [7] and SHELX 76 [8] packages were unsuccessful. The structures were solved by the SIR program [9] through the extensive use of phase semivariants in the starting set. The structures of the compounds (3) and (4) were independently solved by means of heavy-atom techniques using regular and anomalous Patterson maps.

The analysis clearly showed the existence of two different sites occupied by metal ions in the structures.

In all four structures the ATP molecule is bonded to one of the metal ions by oxygen atoms from the α-, β- and γ-phosphate groups. There is no bonding interaction between the metal ions and the adenine base.

The structure analysis of the compounds (1) and (2) showed the presence of a twofold orientational disorder of the DPA molecules.

Further work is in progress to establish the remaining details of the structures.

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T18

Macromolecular Nature of Nucleic Acids in Metal Interactions

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The conformational changes of nucleic acid macromolecules as a result of rotation around C–C, C–O, C–N covalent bonds occur without destruction of the chains, but they can lead to the loss of biological function; this can be seen in interactions with metal ions of nucleic acids. The latter are ambidentate ligands and supply by complex formation different sites of binding, sometimes cooperatively, in polyfunctional chains. This leads to the formation in nucleic acid macromolecules of different coordination centers, among them the unsaturated, deformed type: pure phosphate, mixed phosphate-base, pure base, crosslinked base, sandwich, complementary paired base and others. The probability of the centers is discussed.

As a result of complex formation with nucleic acid macromolecules there are mutual influences between functional groups of the chain, those of electronic origin, conjugations, field effects, dispersion interactions, hydrogen bonding, solvation, supermolecular structure formation and so on.

The interactions mentioned can not so far be expressed in quantitative ways nor can their contributions to equilibrium constants of macromolecular complex formation be written explicitly, therefore the way of describing polymeric complexing systems is through the use of averaged values.

Various examples of the interactions of metal ions with macromolecular chains of DNA and RNA, pH-dependence, conformational changeability and reversibility, as well as the possibility of modelling the macromolecules under study are given.

T19

A Rapid Kinetic Study of Divalent Metal Interactions with Flavin Coenzymes

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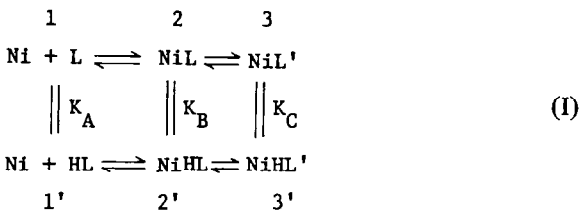
Research in these laboratories has focussed in recent years on the kinetics of divalent metal ion interactions with coenzymes. The principal kinetic tool has been temperature-jump relaxation spectroscopy. A large amount of kinetic information is now available for several nucleotides (*e.g.* AMP) and inorganic phosphates.

The purpose of this paper is to report the first rapid kinetic study of the mechanism of divalent metal ion interactions with the coenzymes flavin mononucleotide (FMN) and flavin adenine dinucleotide (FAD). The two compounds are structurally related to each other as well as to other coenzymes and phosphates that we have previously studied. FAD, for example, is structurally a combination of riboflavin phosphate and adenosine monophosphate (AMP). Ni(II) was chosen as the metal ion for these studies because of the large body of kinetic information that is already available for that ion. It can serve as a useful representative of divalent transition metal ion interactions with these and related coenzymes.

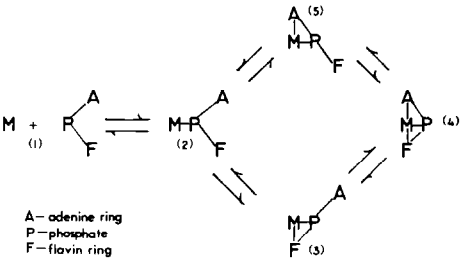
The Ni–FMN system. Two relaxation effects were observed in the kinetic experiments: one (τ_1) on the order of 0.2 msec, the other (τ_2) at about 2 msec. The detailed concentration and pH dependencies of τ_1 and τ_2 are quite similar to those for the relaxation times found in the Ni-ribose phosphate and Ni–AMP systems respectively. The mechanism consistent with these observations is a dual-pathway, back-bound complex mechanism, shown schematically as I:



(I)

in which NiL is the phosphate-bound complex, NiL′ the phosphate + base bound complex.

The Ni–FAD System. FAD presents a number of different binding sites in the ionized phosphate bridge and the base nitrogens on both the adenine and isoalloxazine rings. The flexibility of this molecule facilitiates both individual and simultaneous ring interactions with the phosphate-bound metal. The Ni–FAD system is unique in that *four distinct* relaxation times, τ_1–τ_4, were found and characterized. The relaxation times ranged from 90 μsec to 20 msec and were found to be only slightly pH and concentration dependent. Based on the large body of prior data from our laboratory on simple nucleotide systems, we were able to associate specific relaxation times with reaction steps in scheme II and to determine the rate constants.



(II)

The mechanism shown as II quantitatively accounts for the number and behavior of all the relaxation steps.

In this scheme, F, P and A refer to the flavin, phosphate, and adenine moieties of the FAD molecule, respectively. The first step (1–2) involves bridging to the phosphate moiety only, followed by species involving interactions with the phosphate plus the flavin (5) or adenine moieties (3). The final complex (4) involves simultaneous interactions with all the components of the molecule.

T20

The Copper(II) Promoted Hydrolysis of Salicyl Phosphate (2-Carboxyphenyl Dihydrogen Phosphate)

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One of the striking observations of biological phosphate chemistry is that much of it appears to be