research, but we should emphasize that they are in no way responsible for its deficiencies either in the experiments or our interpretation of the results. We also appreciate the myxobacter 495 culture supplied by Dr. Hunkapiller, from which the auxotroph was derived.

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EPR and NMR Combined Analysis of the Metal–ATP Interaction

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Abstract: The Mn(II)–ATP system has been investigated at the light of new electron spin relaxation findings. A dynamic model, taking into account a distribution of correlation times, is suggested. Namely transverse and longitudinal nuclear relaxation times are analyzed in connection with new values of the electron spin relaxation time. A reinvestigation of NMR and EPR results is tempted as a consequence of the new model. The combined NMR and EPR analysis allows an unambiguous interpretation of nuclear paramagnetic relaxation rates and points out the direct involvement of N(7) in the metal binding.

The metal ion–ATP interaction has been the subject of extensive research,[1-6] due to its relevance in several enzymatic reactions which require nucleoside triphosphate as activator.

Among the various metal ions, Mn(II) has been the most investigated one since Mg(II) ⇌ Mn(II) isomorphous replacement is possible and the Mn(II)–ATP complex has its own biological activity.[7]

Nuclear magnetic resonance,[3-6,8,9] temperature jump,[10] and electron spin resonance[11-13] have been used to elucidate the nature of the interaction both from the structural and the dynamic points of view.

A backbound phosphate–metal ion ring complex has been confirmed by several authors[3,8,9] as the actual substrate for the enzyme. Nevertheless, it is controversial whether the metal ion is water-bridged to N(7) or directly bonded to it.
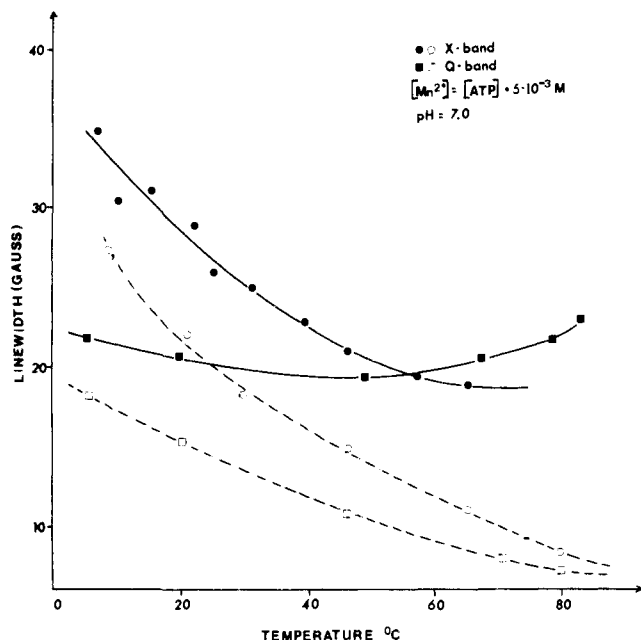
Figure 1. Experimental EPR line width of manganous ion vs. temperature: the dotted curves refer to free hexaaquometal ion; the solid lines refer to $[Mn^{2+}] = [ATP] = 5 \times 10^{-3}$ M aqueous solution.

As is known, there is a close relation between electron and nuclear magnetic relaxation, because the electron spin relaxation time may act as the effective correlation time τ_s in the paramagnetic contribution to nuclear relaxation. Nevertheless, in many cases, electron spin relaxation time has been used without a comprehensive analysis of the EPR spectra and this may result in erroneous interpretations.

On the other hand, recent studies[14,15] on electron spin relaxation of Mn(II) in aqueous solution provided a deeper insight on the dynamics around the metal ion. The aim of this paper is to extend such EPR theory to the Mn(II)-ATP system, suggesting a new dynamic model which accounts for nuclear relaxation rates analysis for both the ligand and the solvent molecules.

The inspection of such a system by means of three independent checks (that is to say, EPR of the metal environment, ^{13}C and ^1H NMR of the ATP molecule, and water-proton relaxation rates) also allows a suitable reinvestigation of the previous results.

Experimental Section

$Mn(ClO_4)_2\cdot 6H_2O$ (Alpha Inorganics) was used in order to minimize anionic complexation. 5'-ATP and D_2O 99.75% were Merck reagent grade and were used without further purification. pH was measured by means of a Metroohm Model E-388 potentiometer.

NMR spectra were recorded with a Bruker WH-90 FT-NMR spectrometer operating at 22.63 MHz for ^{13}C and 90 MHz for ^1H. Temperature was varied by means of the Bruker temperature control unit. Transverse relaxation times were measured from half-height line widths assuming Lorentzian line shape, whereas longitudinal relaxation times were evaluated from partially relaxed proton spectra using $(180-\tau-90-t)_n$ pulse sequences. Care was devoted to the choice of pulse duration.

EPR spectra at both X band and Q band were registered with a Varian V4502 spectrometer.

Temperature was controlled with a conventional variable temperature assembly. All solutions were 5×10^{-3} M in order to avoid the effect of spin-spin interactions on the line shape. The line width parameter was evaluated as the peak-to-peak distance of the first derivative spectrum, measuring the width of the fourth hyperfine line from the low-field side. When appreciable overlapping of the hyperfine components was present, comparison with computer-simulated spectra was made.

The Dynamic Model. The rotational model, rather than the fluctuational one, has been taken into account in order to explain the frequency dependence of electron spin relaxation in a solution of Mn(II).[12,15] The model shows the EPR line width from rotational modulation of the inner product of the quadratic zero field splitting (ZFS) tensor and allows for the existence of a distribution of line widths as a consequence of slow configurational changes of the ionic environment. In fact, typical ZFS values and lifetimes τ_k are obtained for each configuration (including both the first and the second solvation spheres). If the rate of configurational changes τ_k^{-1} is slow with respect to the electron spin relaxation rate (τ_s^{-1}), each ZFS site relaxes as if it was isolated from all others and the resulting spectrum will be the summation of a distribution of spectra. Since τ_k is the mean time for jumps of solvent molecules between the various configurational states, a typical temperature dependence is expected, which must be reflected in the temperature dependence of the electron spin relaxation.

Whenever this situation occurs, a single value of τ_s cannot be assumed and nuclear relaxation rates analysis is not possible in a straightforward way because a distribution of τ_s values must be taken into account. Furthermore, the fitting of temperature dependent experimental nuclear relaxation times, which is usually carried out[3,7,9,11] in terms of the theoretical temperature dependence of fluctuational correlation time τ_v, must be reviewed at the light of the rotational model, because different or even adverse slopes may occur.

Since τ_s is an effective correlation time for scalar interaction, its value affects paramagnetic contributions to nuclear relaxation rates. Namely when $\omega_s\tau_s \gg 1$, scalar contribution to the paramagnetic longitudinal relaxation rate (T_{1p}^{-1}) is negligible whereas it is the dominant one for paramagnetic line width (T_{2p}^{-1}).

On the other hand, whenever $\omega_s\tau_s \ll 1$ an equal scalar contribution is appearing both to T_{1p}^{-1} and T_{2p}^{-1}. All the above statements apply in the fast exchange limit when the lifetime of a nucleus in the metal coordination sphere is short with respect to the relaxation time.

Thus if the τ_s distribution allows a predominance of very short τ_s values, it may happen that a valuable scalar contribution to T_{1p}^{-1} is appearing. Moreover, the simultaneous lengthening of rotational correlation times due to complex species with large molecules may give rise to an effective competition between τ_r and τ_s in determining the dipolar interaction.

Results and Discussion

The following EPR results of the Mn(II)-ATP complex fit the above model: (i) the frequency dependence of the spectra which points out the rotational relaxation mechanism;[12] (ii) the appearance of low-field wings which indicate a distribution of crystal field sites;[12-14] and (iii) the existence of second-order effects on the linewidth which result in typical "inverted" spectra.[12,13]

A further check of the applicability of the dynamic model in the case of the Mn(II)-ATP system is possible from the temperature dependence of the EPR line width.

Figure 1 shows a noticeable difference between the hexaaquomanganese(II) ion and the Mn-ATP system since the line width of the complex displays a smoother decay at X band and even an increase at Q band. As τ_k is expected to be temperature dependent, that is the jump frequency increases when the temperature is raised, the consequent line broadening will oppose itself to the normal narrowing and a resultant line broadening might be expected at higher temperature.

As a consequence of these statements a more suitable picture of the dynamic situation of the Mn(II)-ATP system in solution is possible by means of the above model: the metal ion experiences a distribution of crystal-field sites which results in a distribution of τ_s values.

Despite such EPR interpretation, the nuclear correlation times evaluation has usually been carried out by means of single valued ZFS.[3,9,11]

Also the existence of outer sphere species has never been taken into account in spite of their relevance in the Mn(II)-ATP system.[5] The behavior of the EPR data displayed in Figure 1 and of all the other experimental EPR measurements which we performed on the system (intensity and line broad-
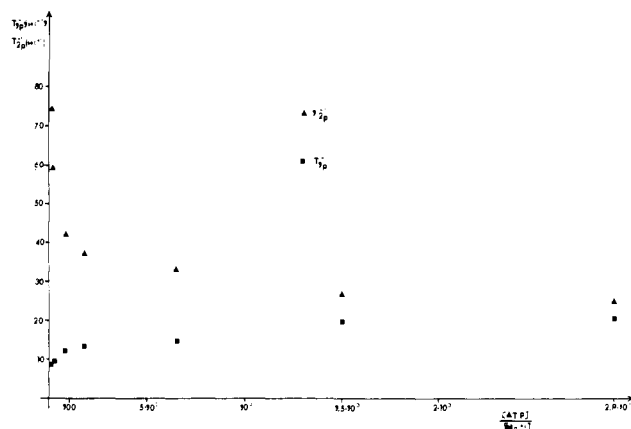
Figure 2. T_{1p}^{-1} and T_{2p}^{-1} of water protons at pH 4 vs. [ATP]/[Mn^{2+}] molar ratios.

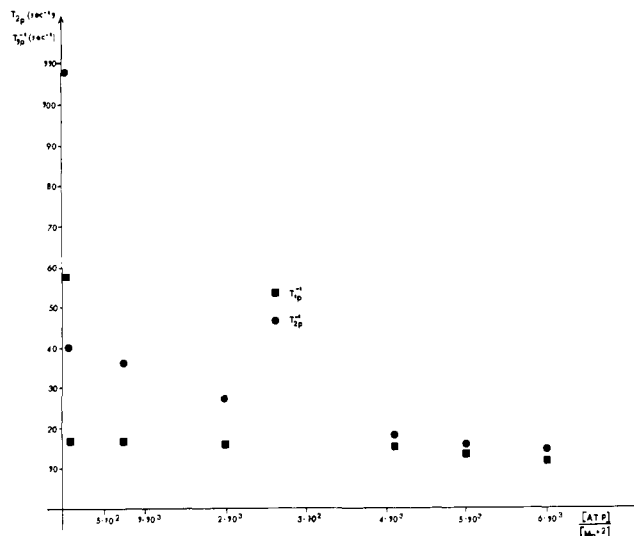**Table I.** NMR Relaxation Rates of a Mn(II)-ATP Complex in Aqueous Solution

nucleus	exchange conditions at rt (pH 7)	paramagnetic contribution	further remarks
^{1}H (ligand)	$T_{1M} \gg \tau_M$	$T_{1p}^{-1} = fT_{1M}^{-1}$	$(fT_{1p})^{-1} \simeq (fT_{2p})^{-1}$
	$T_{2M} \gg \tau_M$	$T_{2p}^{-1} = fT_{2M}^{-1}$	dipolar contribution only or an equal small scalar contribution
^{1}H (water)	$T_{1M} \gg \tau_M$	$T_{1p}^{-1} = fT_{1M}^{-1}$	$(fT_{1p})^{-1} \ll (fT_{2p})^{-1}$
	$T_{2M} \gg \tau_M$	$T_{2p}^{-1} = fT_{2M}^{-1}$	T_{1p}^{-1} dipolar only
			T_{2p}^{-1} scalar only at pH 4 $(fT_{1p})^{-1} \simeq (fT_{2p})^{-1}$
^{31}P	$\tau_M \gg T_{1M}$	$(fT_{1p})^{-1} = (fT_{2p})^{-1} = \tau_M$	exchange controlled relaxation rates; kinetic information is possible
	$\tau_M \gg T_{2M}$		
^{13}C	$T_{1M} \gg \tau_M$	$T_{1p}^{-1} = fT_{1M}^{-1}$	$(fT_{1p})^{-1} \ll (fT_{2p})^{-1}$
	$T_{2M} \gg \tau_M$	$T_{2p}^{-1} = fT_{2M}^{-1}$	T_{1p}^{-1} dipolar only
			T_{2p}^{-1} scalar only

Figure 3. T_{1p}^{-1} and T_{2p}^{-1} of water protons at pH 7 vs. [ATP]/[Mn^{2+}] molar ratios.

Figure 4. fT_{1p}^{-1} of H(8) and H(2) vs. $10^3/T(K)^{-1}$ at pH 4; [ATP] = 10^{-1} M, [Mn^{2+}] = 5 × 10^{-5} M.

ening) definitely points out the existence of outer-sphere species, according to the Eigen-Tamm scheme.[5,16,17]
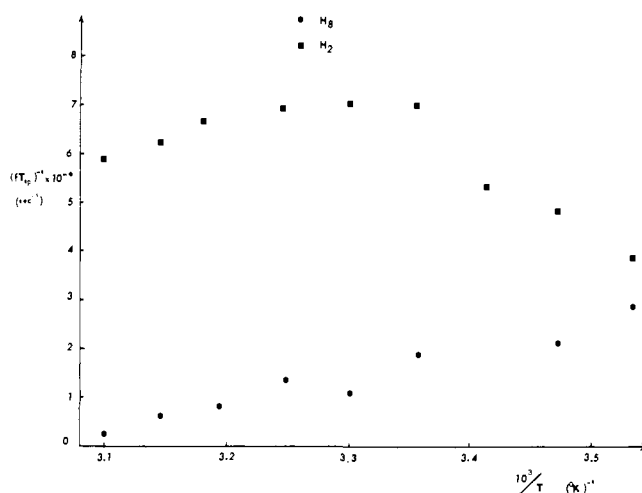
The solvent and ligand dynamics beyond the first solvation shell give rise to small distortion of the crystal field symmetry which results in EPR line broadening. Outer sphere species display typical τ_s values which are shorter by one order of magnitude with respect to that of the hexaaquoion.

The dynamic model resulting from EPR data allows a suitable nuclear relaxation rates analysis. Namely, T_{1p}^{-1} and T_{2p}^{-1} measurements can be performed in various experimental conditions both for the solvent and ligand molecules.

Figure 2 shows the paramagnetic contributions to water protons at various 5'-ATP concentrations at pH 4. It is apparent that before 5'-ATP addition $T_{1p}^{-1} \gg T_{2p}^{-1}$ which reflects a dipolar mechanism for T_1 relaxation and a scalar one for T_2. The presence of ligand molecules results in T_{2p}^{-1} lowering and T_{1p}^{-1} increasing in such a way that at high ATP/Mn(II) ratios the paramagnetic contributions appear to be almost identical. These findings can be explained by a scalar contribution to T_{1p}^{-1} which becomes progressively more important as a consequence of complex species formation which displays a τ_s value such that $\omega_s\tau_s < 1$, whereas the T_{2p}^{-1}

lowering reflects the displacement of water molecules from the coordination sphere.

The same behavior is displayed at pH 7 even if it is less remarkable and no T_{1p}^{-1} increasing is observed (Figure 3).

Different information can be obtained from nuclear relaxation rates analysis on ligand molecules. Figure 4 reports the spin-lattice relaxation rates of the H(8) and H(2) protons in the Mn(II)-ATP system at various temperatures. It may be seen that H(8) is in the fast exchange region till 300 K whereas the H(2) proton is always under fast exchange conditions.

Furthermore, it is possible to compare results with $(fT_{2p})^{-1}$ values reported in the literature.[4] A T_{1p}/T_{2p} ratio longer than 1.17 is apparent so that a scalar contribution to T_{1p}^{-1} can also be suggested in these cases.[18]

The engagement of the theoretical model implies a severe criticism on nuclear relaxation rates analysis because τ_s distribution may result in a random scalar contribution to nuclear relaxation, giving to misleading inferences. A reinvestigation of NMR data is therefore required, as shown in Table I. An inspection of the relative magnitudes of paramagnetic contributions suggests that ^{13}C NMR data are only conclusive from the structural point of view.

In fact, the $(fT_{1p})^{-1} \ll (fT_{2p})^{-1}$ condition (only dipolar contribution to T_1 and only scalar contribution to T_2) holds only for ^{13}C nuclear relaxation as far as the ligand is concerned (Table I). On these bases a comparative analysis of ^{13}C nuclear relaxation rates[3] is more suitable in demonstrating the N(7) involvement in metal binding. Moreover, the selective broadening of the C(5), C(8), and C(4) peaks of ATP, due to purely scalar contribution, points out the direct metal–N(7) bond.[13] These findings are further supported by recent pulsed EPR results.[19]

As conclusive remarks, combined EPR and NMR analysis is very important whenever the binding of large molecules is investigated. Since the manganous ion is widely used as a relaxation paramagnetic probe in biological systems, the following findings must be emphasized: (i) the relevance of outer-sphere species; (ii) the theoretical model for electron spin relaxation which points out the rotational mechanism with its own temperature dependence; and (iii) the existence of several τ_s values which may differ from each other by orders of magnitude, leading to more complicated nuclear relaxation behavior and to a competition with τ_r.

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Covalently Attached Organic Monolayers on Semiconductor Surfaces[1]

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Abstract: Treatment of silicon or gallium arsenide with the refluxing vapors of 3-aminopropyltriethoxysilane in toluene or xylene solution results in a strictly monolayer coverage of the surface with aminopropylsilyl groups. Electron microscopy indicates that these conditions avoid the formation of polymeric globules whose presence is characteristic when the substrate is immersed in the treating solution. Ellipsometric measurement of the thickness change upon reversible adsorption of dodecyl sulfate anions indicates a closely packed layer of extended hydrocarbon chains. This implies that the coverage of the semiconductor surface with the underlying aminopropyl groups is essentially complete. Neither the rate of the silane attachment reaction nor the rate of hydrolysis is strongly affected by the doping level of the semiconductor. Reactions of the amino groups allow bonding of a variety of organic molecules to the surface. Particularly facile are (a) carbodiimide coupling of carboxylic acids, (b) conversion of the surface to a strongly acidic one, and (c) conversion of surface amino groups to isothiocyanate followed by coupling to primary amines.

Reactions of organosilanes with hydroxyl-bearing surfaces have found use in several diverse areas. Linking of molecules of biochemical interest to porous glass, for the purposes of affinity chromatography and enzyme immobilization, have received a great deal of attention.[2-4] The oldest and most widespread use is in promoting the adhesion of polymers to fiberglass.[5-7] More recent interest has centered on electrode modifications,[8-9] catalysis,[10,11] and adhesion promotion in electronic microcircuit processing.[12]

We have investigated some monolayer reactions of organosilanes on surfaces of elemental silicon. One motivation for this was to provide methods for the preparation of chemical systems that can yield information about the interaction between electronic levels of various attached organic moieties and the electronic bands of the semiconductor. Desirable organic moieties would be those that have strong acceptor or donor properties, or carry a permanent ionic charge. Such an interaction, at least in principle, could lead to utilization in solar cells and other semiconductor devices. The reaction of organosilanes on elemental silicon substrates, however, also provides an important and convenient model system for most of the diversely used silanation reactions referred to above. As is well known,[13] freshly etched silicon exposed to air at room temperature is rapidly covered by a thin, coherent oxide layer whose logarithmic rate of growth ensures that in the experimentally accesible time period (1 min to 1 year) the thickness remains in a convenient range (0.5 to 2.5 nm). One expects that the chemical properties of this oxide are not grossly different from bulk silica while it is thin enough to permit tunneling of electrons and thus avoid charging up of the surface in electron microscopy or spectroscopies. The model system is thus free from the disadvantage inherent in fibrous and porous silica or glass substrates whose insulating nature interferes with the utilization of some of the more sophisticated surface analytical techniques. Furthermore, the reflectivity of the underlying silicon substrate allows the use of ellipsometry for the precise