



PS5.17 — TU

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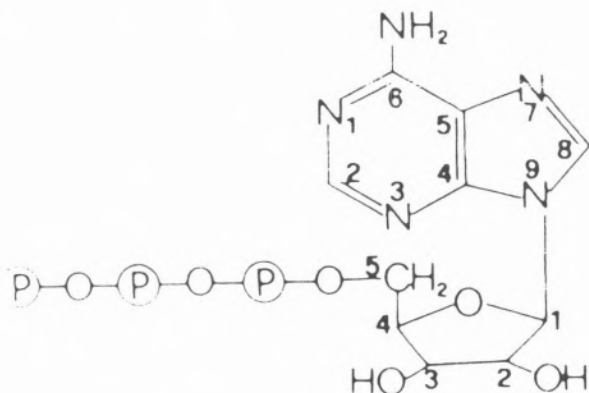
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# **DYNAMICAL PROPERTIES OF ATP/CdCl<sub>2</sub> AND ATP/Cd(ClO<sub>4</sub>)<sub>2</sub> COMPLEXES: A COMBINED <sup>13</sup>C AND <sup>113</sup>Cd RELAXATION STUDY**

In the past and recent years a great deal of investigations were undertaken on the binding mode between ATP and divalent metal ions, especially because of the intrinsic relevant biological importance.



Nuclear Magnetic Resonance has been thoroughly applied in most of these works; however, despite the overall NMR parameters employed, a number of questions on the binding sites on the nucleotide and on the metal ion coordination sphere has still to be answered [1]. Here we present the results of <sup>13</sup>C and <sup>113</sup>Cd spin-lattice relaxation and <sup>13</sup>C-<sup>1</sup>H and <sup>113</sup>Cd-<sup>1</sup>H nuclear overhauser studies of ATP in presence of the diamagnetic salts CdCl<sub>2</sub> and Cd(ClO<sub>4</sub>)<sub>2</sub> (Table 1).

The pertinent data were obtained by means of the following formulas:

$$\frac{1}{T_{1 \text{ obs}}} = \frac{1}{T_{1 \text{ DD}}} + \frac{1}{T_{1 \text{ others}}} \quad (1)$$

$$\frac{1}{T_{1 \text{ DD}}} = \frac{\eta_{\text{obs}}}{\eta_{\text{max}}} \cdot \frac{1}{T_{1 \text{ obs}}} \quad (2)$$

$$\frac{1}{T_{1 \text{ DD}}} = \frac{n_H}{10} \hbar^2 \gamma_X^2 \gamma_H^2 r_{XH}^6 \tau_c \left[ \frac{1}{1 + (\omega_H - \omega_X)^2 \tau_c^2} + \frac{3}{1 + \omega_X^2 \tau_c^2} + \frac{6}{1 + (\omega_H + \omega_X)^2 \tau_c^2} \right] \quad (3)$$

where

$n_H$  = number of relaxators (protons)

$\gamma_X, \omega_X$  = gyromagnetic ratio and angular frequency of the pertinent nucleus (<sup>13</sup>C, <sup>113</sup>Cd) at 1.88 T

$r_{XH}$  = distance of the relaxator from the pertinent nucleus;

Table 1

<sup>13</sup>C Spin-lattice relaxation data and viscosity ( $\eta$ ) measurements of ATP/CdCl<sub>2</sub> and ATP/Cd(ClO<sub>4</sub>)<sub>2</sub> systems in aqueous solution

pH		ATP		ATP/CdCl <sub>2</sub>		ATP/Cd(ClO <sub>4</sub> ) <sub>2</sub>	
		C2	C8	C2	C8	C2	C8
2	$T_1$ (sec)	0.223	0.207	0.095	0.082	0.071	0.067
	$\eta_{\text{obs}}$	2.06	1.97	1.26	1.37	1.22	1.23
	$\eta_{\text{max}}$	1.99		1.99		1.99	
	$T_{1 \text{ DD}}$ (sec)	0.223	0.207	0.150	0.121	0.120	0.108
	$\tau_c$ (sec) <sup>a)</sup>	$1.9 \cdot 10^{-10}$		$3.5 \cdot 10^{-10}$		$4.2 \cdot 10^{-10}$	
	$\eta$ (cp)	1.47		1.58		1.49	
6.5	$T_1$ (sec)	0.203	0.171	0.070	0.058		
	$\eta_{\text{obs}}$	2.06	1.96	1.07	1.13		
	$\eta_{\text{max}}$	1.99		1.99			
	$T_{1 \text{ DD}}$ (sec)	0.203	0.171	0.130	0.103		
	$\tau_c$ (sec) <sup>a)</sup>	$2.3 \cdot 10^{-10}$		$4.1 \cdot 10^{-10}$			
	$\eta$ (cp)	1.57		1.70			

a) Arithmetic averages over the two carbon atoms.

On these basis information was obtained on the dynamics of the complexes and on the number of water molecules coordinated to the metal ion [2,3] (Table 2).

Table 2  
<sup>113</sup>Cd Spin-lattice relaxation data for ATP/CdCl<sub>2</sub> and  
 ATP/Cd(ClO<sub>4</sub>)<sub>2</sub> in aqueous solution

	pH = 2 ATP/Cd(ClO <sub>4</sub> ) <sub>2</sub>	pH = 2 ATP/CdCl <sub>2</sub>	pH = 6.5 ATP/CdCl <sub>2</sub>
T <sub>1</sub> (sec)	1.26	2.37	3.20
η <sub>obs</sub>	-0.45	-0.54	-0.35
η <sub>max</sub>	-2.19	-2.21	-2.19
T <sub>1</sub> DD(sec)	6.13	9.68	20.03
n <sub>H</sub> <sup>a)</sup>	10.2	7.6	3.2

a) Values calculated from eq. (3) with r<sub>Cd-H</sub> = 2.98 Å

It was found that the number of coordinated water molecules strongly depends on the metal ion accompanying counterion (Cl<sup>-</sup> or ClO<sub>4</sub><sup>-</sup>), while the dynamics' data are discussed in terms of increased nucleotide self-association induced by the presence of the metal ion.

## REFERENCES

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PS5.18 — MO

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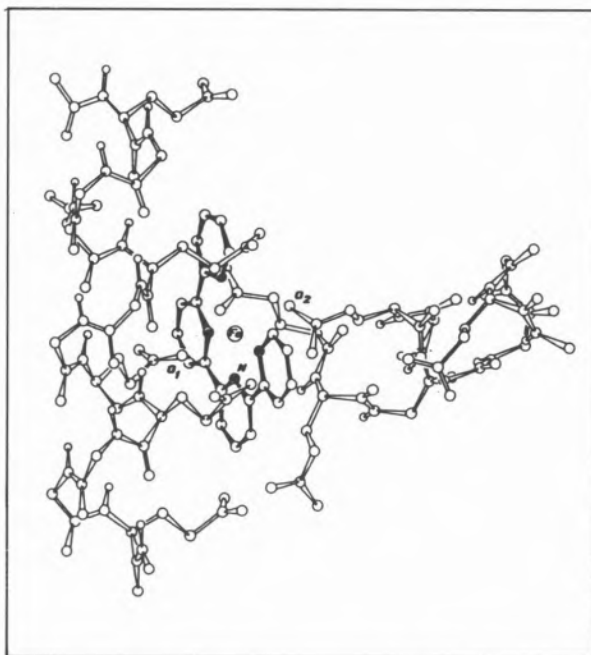
### CHIRAL DISCRIMINATION IN ELECTRON TRANSFER REACTIONS BETWEEN ASYMMETRIC SPECIES

A simple, though realistic, synthetic model of enzymic material for stereoselective oxidation reactions has been prepared by us anchoring hemin-like  $[\text{Fe}(\text{tetpy})(\text{OH})_2]^+$  ions to poly(L-glutamate) (FeTL) or poly(D-glutamate) (FeTD) ( $\text{tetpy} = 2,2',2'',2'''$ -tetrapyridyl) [1,2]. The structural features of FeTL system, under conditions where it exhibits stereoselective activity, are illustrated in Figure. The molecular model was obtained by conformational energy calculations, partially based on available X-ray data, and is fully consistent with a number of experimental findings [3].

Oxidation of chiral catecholamines, such as L-dopa and L-adrenaline, by FeTL and FeTD enantiomeric systems was found to proceed stereoselectively [2], as shown in Table, where thermodynamic data for the formation of the diastereomeric precursor complexes are also reported. From the results, it appears that: i) stereoselectivity is largely controlled by kinetic effects,  $\Delta(\Delta G^\ddagger)$  being definitely higher than  $\Delta(\Delta G^0)$ , and ii) the energetics of chiral discrimination,  $\Delta(\Delta H)$ , is of the order of magnitude that one would have been expected on the basis of  $\Delta(\Delta G^0)$  values, on

the reasonable assumption that the entropies of association of the diastereomeric pairs are nearly identical.

We have also investigated the geometric and steric constraints which control the formation of the diastereomeric adducts by conformational energy calculations, based on nonbonding, electrostatic and hydrogen bonding energy terms [3]. The most relevant molecular parameters of the hypothetical models of the diastereomeric noncovalent electron-transfer complexes, corresponding to the deepest minimum in the total interaction energy, are reported in the same Table. Inspection of the Table indicates that: i) the redox centers in the diastereoisomers experience a different separation distance (and mutual orientation), as one would predict for kinetically-controlled stereoselectivity, ii) the difference in the total energy between LL



and DL pairs agrees surprisingly well (both in magnitude and sign) with the experimentally determined  $\Delta(\Delta H)$  values, and iii) stereoselectivity calculated [3] by the molecular parameters of the models is in satisfactory agreement with that observed.

These findings, and the indirect tests carried out in searching vainly an agreement between calculated and experimental stereoselectivity using molecular parameters corresponding to other relative