

solutions were characterised in terms of two parameters, K and α . K is the selectivity coefficient in the NICOLSKI equation [4] when $\alpha = 1$. Data were collected experimentally and from the literature [5].

In the second stage, experimental titration data for the binding between zinc(II) and the amino acid, cysteine [6,7] were analysed using the ESTA program. Sodium ion interference was found to introduce a systematic error, rising to several millivolts towards the end of each titration. As a result, the first protonation constant of cysteine ($\log \beta_{101} = 10.01$) was lowered by 0.03 log units by omitting from the numerical analysis the effects of sodium ion in the background electrolyte. Larger differences were found for the metal-ligand formation constants (e.g. $\Delta \log \beta_{210} = 0.06$; $\Delta \log \beta_{330} = 0.1$). Generally, the errors were about ten times larger than the calculated standard deviations for the corresponding formation constants.

It may be concluded that significant systematic errors have affected many bioinorganic formation constants determined in sodium ion background electrolyte solutions. However, with modern glass electrodes, the magnitude of these errors is probably about the same as other systematic effects (such as those arising from errors in the analytical concentrations of the solutions being titrated). Nevertheless, they are sufficiently serious to warrant attention in any precise determination of formation constants for bioinorganic purposes.

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PS5.16 — MO

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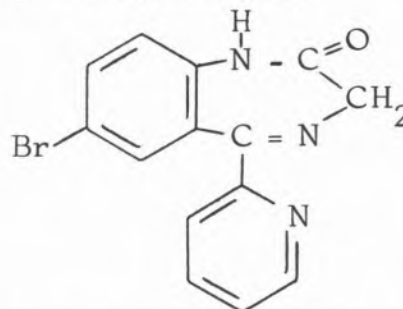
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SYNTHESIS AND CHARACTERIZATION OF d-BLOCK COMPLEXES WITH BROMAZEPAM AS LIGAND

Working in the field of 1,4-benzodiazepines of biological and pharmacological interest as ligands, we report the complexes of ruthenium(III), osmium(III), rhodium(III), iridium(III), palladium(II) and platinum(II) halides with 7-bromo-1,3-dihydro-5-(2-pyridil)-2H-1,4-benzodiazepin-2-one (bromazepam).



These new derivatives, of the ML_3X_3 and MLX_2 type, have been characterized on the basis of elemental analyses, IR and electronic spectra, multinuclear NMR studies, conductivity measurements, magnetic susceptibility data and thermal analyses. These studies suggest a pseudo-octahedral structure for rhodium and iridium derivatives and a square planar geometry for the palladium and platinum ones. The ligand behaves always as bidentate through the nitrogen in 4-position of the diazepine ring and the nitrogen of the pyridine ring.

Assignments for the metal-ligand and metal-halide bands have been made.

The results will be compared with those obtained with other 1,4-benzodiazepines.



PS5.17 — TU

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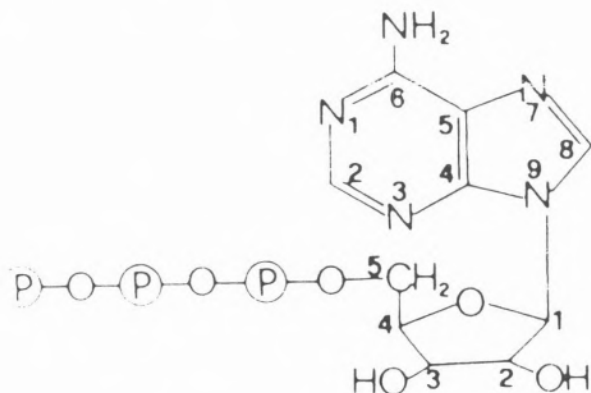
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DYNAMICAL PROPERTIES OF ATP/CdCl₂ AND ATP/Cd(ClO₄)₂ COMPLEXES: A COMBINED ¹³C AND ¹¹³Cd RELAXATION STUDY

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 ¹³C and ¹¹³Cd spin-lattice relaxation and ¹³C-¹H and ¹¹³Cd-¹H nuclear overhauser studies of ATP in presence of the diamagnetic salts CdCl₂ and Cd(ClO₄)₂ (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)

γ_X, ω_X = gyromagnetic ratio and angular frequency of the pertinent nucleus (¹³C, ¹¹³Cd) at 1.88 T

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

Table 1

¹³C Spin-lattice relaxation data and viscosity (η) measurements of ATP/CdCl₂ and ATP/Cd(ClO₄)₂ systems in aqueous solution

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