

(i) at pH 4 by addition of DNA, Fe(III)·BLM is converted into a low spin species which rapidly decays. On the other hand, the addition of ligands (L) such as N_3^- , SCN^- , $\text{S}_2\text{O}_3^{2-}$ to Fe(III)·BLM yields brightly colored complexes in the low spin form.

(ii) at pH 7 the same colored complexes BLM·Fe(III)·L are obtained by addition of an excess of L. The addition of DNA to these complexes gives rise to the release of L and an BLM·Fe(III)·DNA complex is obtained.

These experiments strongly suggest that the various ligands: the α amino group of BLM, N_3^- , SCN^- , $\text{S}_2\text{O}_3^{2-}$ or ADN are competing ligands for the apical position A.

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VII

Metal Ion Interaction with Ribavirin (1- β -D-ribofuranosyl-1,2,4-triazole-3-carboxamide)

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The antitumor agent cis Pt^{II}(NH₃)₂Cl₂ is known to interact with guanine with possible binding to the 6-oxo group, promoting deprotonation on N(1) [1]. N(4)-O(7)-Cu(II)-ribavirin chelate has been demonstrated [2] in a solid state and these particular binding sites were assumed also for other ribavirin-Me(II) interactions in solution.

Even a single crystal-X-ray analysis assumed a conformation of ribavirin strikingly similar to guanosine [2]. This resemblance prompted further studies of ribavirin Pt(II) complexes as Pt(II) complexes are convenient to compare solid state and solution properties of these chelates. The binding of the paramagnetic Cu⁺⁺ ion to ribavirin in solution was located mainly on N(5) by ¹H and ¹³C line broadening and T₁ relaxation times and did not support any binding on exocyclic oxygen O(7).

The role of the carboxamide group in metal binding to ribavirin is thus not completely clear. Pt(II)-complexing will be discussed in order to clarify this question, as well as ¹⁴N relaxation of the carboxamide nitrogen. In this case, the indirect measurement of ¹⁴N relaxation rates is possible. T_{1ρ}

(spin-locking method) eliminates effects on proton relaxation other than proton-nitrogen scalar coupling. Thus T_{1N} and A (¹⁴N-coupling) of amino protons will be evaluated from the following equation:

$$\frac{1}{T_{1\rho}(\text{obs})} - \frac{1}{T_1} = \frac{2}{3} A^2 \frac{T_{1N}}{1 + \omega_1^2 T_{1N}^2}$$

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VII2

Metal Ion Interaction with Inducers of Reverse Transformation of Cancer Cells

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Gosálvez, based on a theoretical hypothesis of the function of the plasma membrane, designed three heterocycles as possible inducers of reverse transformation of cancer cells to normal phenotype [1]. Two of these compounds (thiaproline, TP, and 2-amino-1,3-thiazoline, AT) have been taken to the anticancer clinics and have shown, preliminarily, an antitumor activity [2].

Both ligands are believed to bind in the lipid environment a zinc ion linked to a protein complex of the membrane, which would be the origin of macrofilaments [3].

In this communication the NMR, spectroscopic and X-ray results for the Cu(II), Cd(II) and Zn(II) complexes with the above mentioned ligands are discussed to establish possible binding modes of these ligands with metal ions.

Both ligands are unstable in aqueous solution at pH > 6 and their decomposition is additionally promoted by the presence of metal ions [4].

In acidic solution the AT ligand does not interact directly with the studied metal ions, but it acts as cation ATH⁺.

The protonation site, established by X-ray technique, is the heterocyclic nitrogen which appears to be quite a basic donor.

The most 'destructive' metal ion seems to be the cupric ion, which due to the redox reaction leads to several different decomposition products of AT, including SO₄²⁻ and [NH₂⁺CH⁻NH₂]⁺Cl⁻ [5].