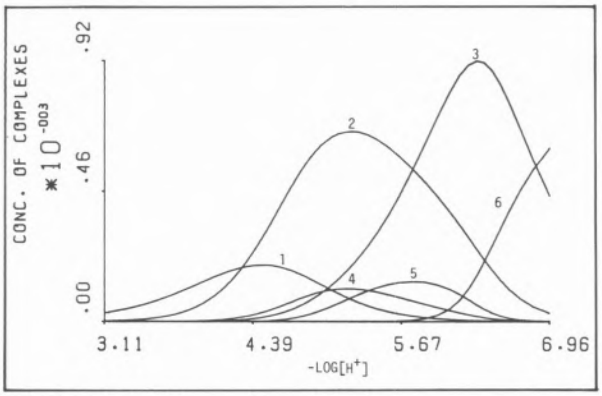

Figure

Concentrations of complexes present as a function of pH for the caffeic acid-copper (II) system when the total concentrations in mmol dm^{-3} *of* L^{2-} *and* Cu^{2+} *are 8.6 and 2.0, respectively. Temperature=25°C and* $I=0.100$ *mol* dm^{-3} *(Na) [Cl]. Species: (1)* $LCuH^{+}$*; (2) LCu; (3)* $(LH_{-1})Cu$*; (4)* $(LH_{-1})Cu_2$*; (5)* $(LH_{-1})_2Cu_3$*; (6)* $(LH_{-1})_3Cu_2$

as being plausible. (1) $LCuH^{+}$: copper coordinated to the carboxylate; (2) LCu and (3) $(LH_{-1})Cu$: copper coordinated to the catechol moiety; (4) $(LH_{-1})Cu_2$: one copper at each end of the molecule; (5) $(LH_{-1})_2Cu_3$ and (6) $(LH_{-1})_3Cu_2$: oligonuclear species with copper acting as bridges between adjacent caffeate moieties.

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PS5.34 — TU

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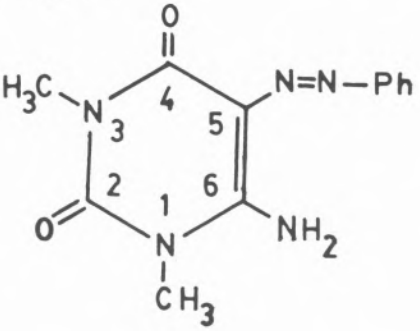
INTERACTION OF 6-AMINO-1,3-DIMETHYL-5-PHENYLAZOURACIL WITH Co(II), Ni(II), Cu(II) AND Ag(I) IONS

INTRODUCTION

Compounds containing pyrimidine rings are widely distributed in living cells and play a significant role in many biological systems (the ring system being an integral part of several nucleic acids, vitamins, etc.); these facts have stimulated research into the coordination modes of pyrimidines, in order to know the role of metal ions in such systems [1-4]. As an arylazo group is of interest in promoting potential antineoplastic activity [5], the pyrimidine molecules having an arylazo group are of interest. For this reason and as part of our work on the interaction of pyrimidine-derived ligands with metal ions [6-9], in the present paper, the synthesis, spectroscopic characterization and thermal behaviour of the 6-amino-1,3-dimethyl-5-phenylazouracil (DZH) and its Co(II), Ni(II), Cu(II) and Ag(I) complexes have been investigated.



DZH

EXPERIMENTAL

DZH was synthesized according to Rose [10], using 6-amino-1,3-dimethyluracil and phenylamine as starting materials.

IR and ^1H-NMR spectra were recorded on a Beckman 4250 spectrophotometer and a Hitachi-Perkin Elmer R-600 FT-NMR spectrometer. Thermal studies were carried out on a Mettler TG-50 thermobalance and a Mettler differential scanning calorimeter model DSC-20.

The complexes $Co(DZ)_2NO_3.H_2O$; $Ni(DZ)_2$; $Cu(DZ)NO_3.H_2O$ and AgDZ were obtained by mixing an ethanolic solution containing 0.4 mmoles of DZH with an ethanolic solution of the respective metal nitrate (0.20 mmoles). The mixture was heated at 70-80°C with continuous stirring for about one hour. The resulting clear solution was allowed to cool slowly to room temperature. After a few days precipitates appeared. All the complexes were washed consecutively with water and ethanol and ether dried. $Cu(DZ)_2py$; $Cu(DZ)_2DMSO$ and $Cu(DZ)_2.2H_2O$ were obtained using the above experimental method, but pyridine, dimethylsulfoxide and 1:1 ethanol-NH_4OH mixture were used as solvents, respectively.

RESULTS AND DISCUSSION

From spectroscopic data it can be suggested that, in solid phase, DZH is in amine-ketonic form (scheme I) (bands at 3290 and 3260 cm^{-1}, corresponding to ν(N-H) of the amine group and 1705 and 1610 cm^{-1} due to $\nu(C_2=O)$ and $\nu(C_4=O)$, respectively). However, in the isolated complexes, the anjon DZ is coordinated to metal ions in imino-phenolic form, since IR spectra show only one band ν(N-H), as well as a new ν(C=N) band, both corresponding to the iminic group.

On the other hand, the ν(N=N) band is shifted towards lower frequencies upon metal complexes formation, which suggests that a nitrogen atom of the diazo group is involved in the coordination, probably the one joined to the phenyl group, since the ν(C-N) band is also shifted towards lower frequencies. Likewise, the IR spectra of the complexes show bands in the region 435-420 cm^{-1}, which are not observed in the ligand spectrum; these bands are attributed to ν(M-O) vibration (oxygen atom joined to C_4).

Elemental analysis, magnetic measurements and spectral studies [11] suggest the following molecular structures for the isolated complexes: $[Co(DZ)_2(H_2O)_2]NO_3$ (distorted octahedral); $Ni(DZ)_2$ (tetrahedral); $Cu(DZ)(H_2O)NO_3$ (tetrahedral with a monodentate nitrate group); Ag(DZ) (linear polymeric); $Cu(DZ)_2(H_2O)_2$ (distorted octahedral); $Cu(DZ)_2py$ and $Cu(DZ)_2DMSO$ (square-pyramidal).

The thermal behaviour of these complexes has been studied by IR, TG and DSC. IR spectroscopy applied to the study of the complexes heated at 225°C allowed to clarify the decomposition steps and the nature of the intermediate products.

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PS5.35 — TH

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COMPARATIVE STUDY OF METALLOCHLORINS AND METALLOPORPHYRINS BY RESONANCE RAMAN SPECTROSCOPY

Basic studies on metallochlorins have recently become increasingly important, because it was found that not only chlorophylls but also some hemoproteins contain the metallochlorin as a prosthetic group (*e.g.* [1]). In order to elucidate the reason for the existence of chlorin prosthetic groups in some hemoproteins it is essential to investigate what features of molecular and electronic structures of metallochlorins are different from those of metalloporphyrins. Thus we have undertaken comparative study of metallochlorins and metalloporphyrins using resonance Raman (RR) spectroscopy [2] which is known to be a powerful structure probe for hemoproteins as well as their model compounds [3,4].

RESULTS AND DISCUSSION

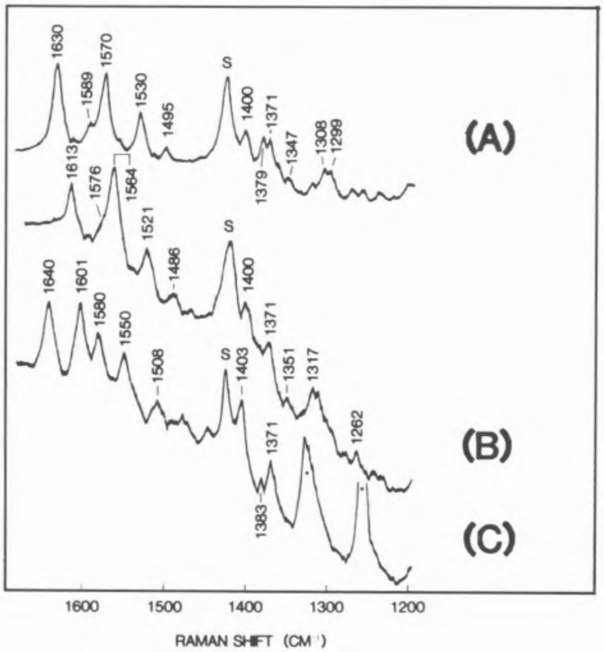

Fig. 1

Resonance Raman spectra of (A) Fe(OEC)Br, (B) Fe(OEC)(Me_2SO)$_2$, and (C) Fe(OEC)(Im)$_2$Br.

Experimental conditions: excitation wavelength, 488.0 nm; laser power, 200 mW; spectral slit width, 6 cm^{-1}. S denotes Raman lines due to solvents (CH_2Cl_2 for Fe(OEC)Br and Fe(OEC)(Im)$_2$Br and 1:1 mixture (V/V) of CH_2Cl_2/Me_2SO for Fe(OEC)(Me_2SO)$_2$). Bands marked with an asterisk are due to imidazole

Fig. 1 shows the 488.0 nm-excited RR spectra of Fe(OEC)Br (5-coordinate, high-spin; OEC = octaethylchlorin), Fe(OEC)(Me_2SO)$_2$ (6-coordinate, high-spin; Me_2SO = dimethyl sulfoxide), and Fe(OEC)(Im)$_2$Br (6-coordinate, low-spin; Im = imidazole). RR bands at 1630, 1570, and 1494 cm^{-1} of Fe(OEC)Br can be assigned to the modes involving mainly the methine bridge stretching vibration, that is, ν_{10}, ν_{19}, and ν_3 modes [2], respectively. These frequencies are very close to those of the corresponding modes of Fe(OEP)Br. Since the frequencies of ν_{10}, ν_{19}, and ν_3 modes are correlated with the center-to-pyrrole-N distance of the porphyrin cavity [4], the close similarities in the frequencies of these modes between Fe(OEC)Br and Fe(OEP)Br indicate the similarity in their core sizes. RR bands of Fe(OEC)Br at 1589 and 1530 cm^{-1} may be due to the modes involving substantially the $C_\beta C_\beta$ stretching character [2]. The corresponding modes of Fe(OEP)Br were observed at 1581 and 1558 cm^{-1}. Although it was expected that the two $C_\beta C_\beta$ stretching modes would show large downward shifts upon saturation of one of $C_\beta C_\beta$ bonds, the 1581 cm^{-1} band did exhibit an upward shift by 8 cm^{-1}. Two $C_\beta C_\beta$ stretching modes of Fe(OEP)Br with