

THERMAL BEHAVIOUR OF SILVER(I) COMPLEXES OF 4-AMINO-5-NITROSO-URACIL DERIVATIVES

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The silver(I) complexes of 4-amino-5-nitroso-uracil, 4-amino-1-methyl-5-nitroso-uracil, 4-amino-3-methyl-5-nitroso-uracil and 4-amino-1,3-dimethyl-5-nitroso-uracil have been prepared and their thermal behaviour studied. All the isolated compounds show 1:1 stoichiometry.

It is known that metal complexes of pyrimidines and their nucleotides play a dominant role in many biochemical systems [1,2]. In recent years a large number of metal complexes of pyrimidine derivatives have been isolated [3–5]. However, there is no report in the available literature about the thermal behaviour of these complexes. This note reports the thermal decomposition of the complexes of Ag(I) with 4-amino-5-nitroso-uracil (A–H), 4-amino-1-methyl-5-nitroso-uracil (B–H), 4-amino-3-methyl-5-nitroso-uracil (C–H) and 4-amino-1,3-dimethyl-5-nitroso-uracil (D–H).

Experimental

The pyrimidine derivatives were prepared by methods previously reported [6] and the silver complexes were obtained as follows:

Ag(A).H₂O and Ag(B).H₂O: An aqueous solution (5ml) of AgNO₃ (4 mmol) was added slowly with stirring to a hot aqueous solution (200 ml) of the corresponding ligand (2 mmol). The complexes precipitated immediately and, after stirring for half an hour, were filtered off, washed with H₂O and ethanol and dried with ethyl ether.

Ag(C): An aqueous solution (5 ml) of AgNO₃ (4 mmol) was added (slowly with stirring) to a hot ethanol solution (200 ml) of C–H (2 mmol). After a few days a pink solid was precipitated. This compound was filtered off, washed and dried as before.

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Ag(D): The synthesis of this compound was carried out by the same method, with the simultaneous addition of ammonium hydroxide (to pH 8) to the resultant solution. The product precipitated immediately and, after stirring for thirty minutes, was filtered off, washed with H₂O and ethanol and dried with ethyl ether.

The silver(I) complexes prepared, along with their elemental analysis and reflectance spectra data, are presented in Table 1.

Thermogravimetric analyses were made in air with a Mettler TG 50 thermobalance at a heating rate of 10 deg.min⁻¹, whereas the DSC runs were carried out on a Mettler DSC-20 differential scanning calorimeter at a heating rate of 5 deg.min⁻¹. The thermal reactions were obtained with samples varying in weight from 1.77 to 8.74.

Results and discussion

The TG and DSC plots of the isolated silver(I) complexes are given in Figs 1 and 2. From these two Figures, the dehydration and decomposition temperatures, the observed weight losses, the calculated weight losses based on the formation of Ag⁰, as well as the DSC peak temperatures and dehydration energies have been calculated. The results obtained are included in Table 2.

In the case of Ag(A).H₂O a weight loss started at 125^o and finished at 190^o (6.9% total weight loss), which corresponds to one water molecule. The expected endothermic behaviour for the dehydration process associated with this weight loss was observed from the DSC curve in the same temperature range. The necessary energy for the total dehydration, calculated from DSC plots, was 43.0 kJ.mol⁻¹. The anhydrous compound is stable up to about 300^o. Then, an abrupt weight loss occurred in the range 300–360. From 360^o to 520^o there was finally a slow weight loss. On the basis of its elemental analysis and IR spectrum, the weight of the sample remaining at the end of the pyrolysis corresponded to metallic Ag.

The complex Ag(B).H₂O became completely dehydrated in the range 100–190^o. The observed weight loss in the above temperature range corresponded to one molecule of water. The dehydration enthalpy calculated from the DSC curve (Fig. 2) was 56.9 kJ.mol⁻¹. This value suggests that the water molecule in Ag(B).H₂O is slightly more strongly linked to the metal ion than in Ag(A).H₂O. The anhydrous complex is stable in the range 190–240^o. From 240^o the decomposition of Ag(B) to metallic silver took place in four steps, as we can see in the DTG curve. The residue obtained after the fourth step was assigned to Ag⁰ on the basis of its weight loss and IR spectral studies.

Ag(C) showed no weight loss up to about 267^o. At this temperature a very rapid decomposition occurred, corresponding to a 36.7% weight loss. After this vigorous reaction, a slow decomposition started, which finished at about 600^o. The total weight loss at the end of the pyrolysis (62.0%) indicated the formation of metallic silver, as in the previous cases. The DSC curve of Ag(C) shows the anhydrous character of the isolated compound. In this curve (Fig. 2c) the exothermic effects associated with the weight losses were observed in the same temperature range as in TG and the corresponding decomposition enthalpies are shown in Table 2.