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Metal Binding at N_1 and N_7 in a Silver Nitrate–9-Methyladenine Complex

C. GAGNON and A. L. BEAUCHAMP

Department of Chemistry, University of Montreal, C.P. 6210, Succ. A, Montréal, H3C 3V1, Québec, Canada

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Silver ions bind primarily to the base portion of nucleic acids.[1] On the basis of uv spectra and potentiometric measurements, it was concluded that displacement of an amino hydrogen atom by silver ions takes place in neutral or alkaline solutions. Additional interactions of the metal with ring nitrogen atoms were assumed by Davidson *et al.*[2] in order to explain the polymeric character of the products obtained. On the other hand, chelate formation *via* N_7 and the amino group was postulated for adenosine from solution equilibrium data on slightly acidic solutions.[3]

By reaction of silver nitrate with 9-methyladenine in dilute nitric acid (pH ~ 3), crystal of the 1:1 compound $AgNO_3 \cdot$9-Methyladenine$\cdot H_2O$ were obtained. They belong to space group $P2_1/c$ with the following cell parameters: a = 14.41, b = 7.397, c = 23.36 Å and $\beta = 122.13°$. There are eight formula units per cell or two per asymmetric unit. The structure was solved from 2100 unique observed reflections and isotropically refined to a conventional R factor of 0.079. At the moment, the positions of both silver atoms and ligand molecules have been unambiguously determined. The nitrate groups and water molecules appear to be disordered, but that situation does not affect the metal ion and ligand positions.

Figure 1 shows the basic unit (two Ag^+ ions and two ligands) of the infinite cationic chain found in the crystal. Each silver atom is digonally bound to N_1 of one ligand and to N_7 of the following ligand. Each ligand bridges two silver atoms so that N_1 and N_7 are both involved in complexation. The Ag–N distances (2.14 - 2.21 Å) indicate equally strong bonds with both types of nitrogens. Some of the nitrate oxygens are also found around silver. Their exact positions cannot be discussed at the moment because of the disorder, but they appear to interact only very weakly with the metal, as often observed in digonally coordinated Ag(I) and Hg(II) compounds.

From a large number of recent crystallographic studies, N_7 has been identified as the most common complexation site in N_9-substituted adenines. So far, X-ray evidence for simultaneous interactions at N_1 and N_7 has been reported only for $CoCl_2 \cdot$9-Methyladenine,[4] a compound obtained from ethanol solutions. The present structure failed to show interactions with the amino group, but the substitution proposed[1,2] for neutral and alkaline solutions would probably not take place in acidic media, where our compound was isolated. Consequently, the possibility of amino hydrogen substitution at higher pH is not ruled out, but the present work points out that N_1 may be an important reaction site for Ag^+ ions, as in the case of CH_3Hg^+.[5]

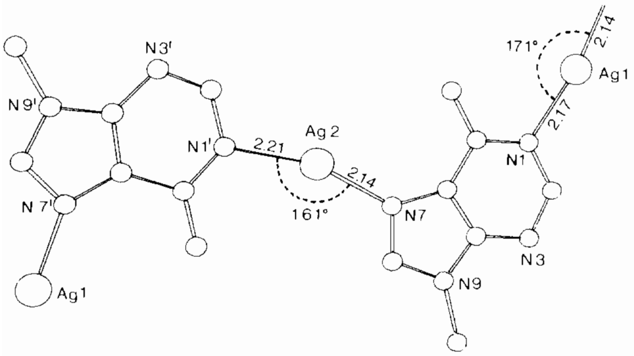

Fig. 1. Basic unit of the polymeric chain $-Ag^+-L-Ag^+-L-Ag^+\cdots$ found in the crystals.

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