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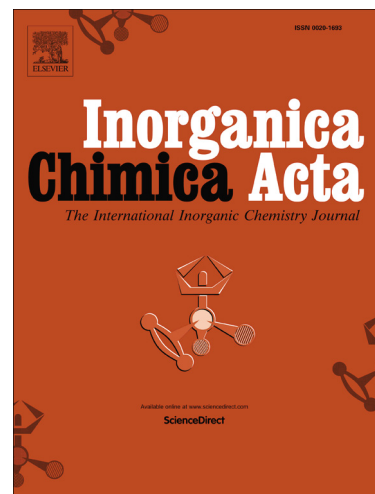
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A Dinuclear Silver(I)-Mediated Base Pair in DNA Formed From 1,*N*⁶-Ethenoadenine and Thymine

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ABSTRACT

The artificial nucleobase 1,*N*⁶-ethenoadenine (ϵ A) is shown to form a dinuclear Ag(I)-mediated base pair with a complementary thymine (T) residue in double-helical DNA. The stabilizing effect brought about by the formation of such a metal-mediated base pair amounts to 5 – 6 °C. It does not depend on the orientation of the base pair within the duplex, i.e. the ϵ A–Ag(I)₂–T base pair confers the same stability as the T–Ag(I)₂– ϵ A base pair. Circular dichroism studies and temperature-dependent UV spectroscopy were applied to establish the formation of this Ag(I)-mediated base pair. Based on DFT calculations, a base pair configuration is proposed in which one Ag(I) ion is coordinated by ϵ A–N6 and T–O4, whereas the other Ag(I) ion forms coordinate bonds to ϵ A–N7 and T–N3. The computations indicate a short intramolecular Ag...Ag contact of 2.87 Å, suggesting that argentophilic interactions may be involved.

Keywords: bioinorganic chemistry, nucleic acids, silver, metal-mediated base pair

Dedicated to Professor Imre Sóvágó on the occasion of his 70th birthday.

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