

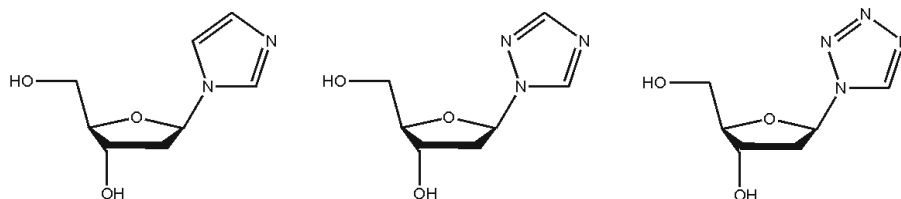
Metal Ion Coordination to Azole Nucleosides

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In the past few years, the interest in replacing the naturally occurring nucleobases in DNA by related base surrogates has increased dramatically. Synthetic base pairs used so far rely on either hydrogen bonding,^[1] hydrophobic interactions^[2] or metal ion coordination.^[3] These orthogonal base pairs might be useful for extending the genetic code. Especially metal ion containing nucleic acids hold great promise as self-assembled molecular devices with interesting properties such as electrical conductivity, magnetism, or the capability of information storage.

In an effort to increase the spectrum of known metal-mediated base pairs,^[4] we have prepared and characterized imidazole nucleoside, 1,2,4-triazole nucleoside and tetrazole nucleoside and determined their metal ion coordination behavior with respect to the linearly coordinating ions Ag^+ and Hg^{2+} . The β nucleosides display $\text{p}K_{\text{a}}$ values of 6.01, 1.32 and <-1 , respectively. The stability of their metal ion complexes decreases accordingly. Whereas imidazole nucleoside forms highly stable 2:1 complexes feasible for incorporation into artificial oligonucleotides, tetrazole nucleoside only form a 1:1 complex (K_{ass} for the Ag^+ complex: $7.3 \pm 0.3 \text{ M}^{-1}$) under the experimental conditions used. DFT calculations show that the glycosidic bond distance in an imidazole- $\text{M}^{\text{n}+}$ -imidazole base pair closely resembles that of Watson-Crick base pairs in B-DNA (10.8–11.0 Å vs. 10.85 Å).



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