Noncanonical Metallo-Base Pairs

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High-Resolution Crystal Structure of a Silver(I)–RNA Hybrid Duplex Containing Watson–Crick-like C–Silver(I)–C Metallo-Base Pairs

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Abstract: *Metallo-base pairs have been extensively studied for applications in nucleic acid-based nanodevices and genetic code expansion. Metallo-base pairs composed of natural nucleobases are attractive because nanodevices containing natural metallo-base pairs can be easily prepared from commercially available sources. Previously, we have reported a crystal structure of a DNA duplex containing T–Hg^{II}–T base pairs. Herein, we have determined a high-resolution crystal structure of the second natural metallo-base pair between pyrimidine bases C–Ag^{I}–C formed in an RNA duplex. One Ag^{I} occupies the center between two cytosines and forms a C–Ag^{I}–C base pair through N3–Ag^{I}–N3 linear coordination. The C–Ag^{I}–C base pair formation does not disturb the standard A-form conformation of RNA. Since the C–Ag^{I}–C base pair is structurally similar to the canonical Watson–Crick base pairs, it can be a useful building block for structure-based design and fabrication of nucleic acid-based nanodevices.*

Metal-mediated base pairs, which are also called metallo-base pairs, are currently receiving considerable attention because of their potential in nanobiotechnology.[1] For example, several metallo-base pairs composed of natural and artificial nucleobases have been applied to nucleic acid-based nanodevices, such as metal ion sensors,[2] electric transport nanowires,[3] and molecular magnets.[4] We have been especially focusing on the metallo-base pairs composed of only natural nucleobases, since nucleic acids containing such base pairs can be easily prepared from commercially available sources. The first metallo-base pair composed of natural nucleobases found in DNA duplex is a T–Hg^{II}–T base pair.[5] Very recently, more than a half century after discovery of the natural metallo-base pair,[5a] tertiary structures of DNA duplexes containing the T–Hg^{II}–T base pairs have been finally solved by our X-ray and NMR studies.[6] The first natural metallo-base pair found in RNA duplex is a G–Au^{III}–C base pair, which was incidentally obtained by heavy metal soaking into crystals of the HIV-1 RNA dimerization-initiation site,[7] though specificity between Au^{III} and the Watson–Crick G=C base pair is not well understood and occupancy of Au^{III} is only 0.35.

Our discovery of the next metallo-base pair composed of natural nucleobases, a silver-mediated C–C base pair (C–Ag^{I}–C), expanded the possibilities for application of natural metallo-base pairs to nanobiotechnology.[8] We have observed by melting temperature analyses that Ag^{I} significantly stabilizes a DNA duplex $d(A_{10}CA_{10})/d(T_{10}CT_{10})$ containing a CC mismatch at the center. However, other metal ions tested (Hg^{II}, Cu^{II}, Ni^{II}, Pd^{II}, Co^{II}, Mn^{II}, Zn^{II}, Pb^{II}, Cd^{II}, Mg^{II}, Ca^{II}, Fe^{II}, Fe^{III}, and Ru^{III}) did not affect the stability of the DNA duplex, suggesting that the CC mismatch selectively captures Ag^{I}.[8] The specific binding of Ag^{I} to the CC mismatch has been confirmed by 1D ^{1}H NMR spectroscopy, CD spectroscopy, electrospray ionization mass spectroscopy, and isothermal titration calorimetry (ITC).[8,9] The ITC-derived binding constant of the complex between Ag^{I} and a DNA duplex containing a CC mismatch is nearly $10^{6}\,M^{-1}$, which is significantly larger than those observed for non-specific interactions between metal ions and DNA (10^{3}–$10^{5}\,M^{-1}$).[9] The 1:1 binding stoichiometry between Ag^{I} and the CC mismatch was also quantitatively determined by the ITC experiment and 1D ^{1}H NMR spectroscopy.[8,9] However, detailed structural information of a nucleic acid duplex containing the C–Ag^{I}–C base pair has long been missing. Herein, we have successfully determined the crystal structure of an RNA duplex containing the C–Ag^{I}–C base pairs at a resolution of 1.3 Å. So far, the C–Ag^{I}–C base pair has been extensively applied for developing several nucleic acid-based nanodevices[10] and for genetic code expansion[11] even without its detailed structural information. The present high-resolution crystal structure of the C–Ag^{I}–C base pair, together with our previously reported crystal and solution structures of the T–Hg^{II}–T base pair[6] open the possibility of structure-based design of nanodevices containing natural metallo-base pairs.

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The RNA dodecamer r(GGACU[dC^{Br}]GACUCC) (RNA-C_4C_9; dC^{Br} = 5-bromo-2′-deoxycytosine), designed to form a self-complementary duplex containing two CC mismatches, was chemically synthesized (Gene Design Inc. Japan) and purified by denatured polyacrylamide gel electrophoresis and reverse phase chromatography. A 5-bromo-2′-deoxycytosine is introduced at the sixth position for resolving the phase problem by the anomalous dispersion method. Needle-shaped and rod-shaped single crystals of RNA-C_4C_9 were grown in conditions with and without Ag^I, respectively (RNA-C_4C_9/Ag^I and RNA-C_4C_9 crystals; Supporting Information, Table S1). To confirm whether linearly coordinating Hg^{II} binds to the CC mismatch or not, the RNA was also crystallized in the presence of Hg^{II}, and rod-shaped single crystals were obtained (RNA-C_4C_9/Hg^{II} crystal; Supporting Information, Table S1). These crystal structures are deposited in the Protein Data Bank (PDB) with the ID codes 5AY2, 5AY3, and 5AY4 (Supporting Information, Table S2). Details of materials and methods are found in the Supporting Information.

In the RNA-C_4C_9/Ag^I crystal, an asymmetric unit was composed of two RNA duplexes (Supporting Information, Figure S1 a). These duplexes are almost identical to each other (Figure S1 b). At the center and both ends of these duplexes, the canonical Watson–Crick G≡C and A–U base pairs are formed. At the fourth and ninth positions of these duplexes, Watson–Crick-like C–Ag^I–C metallo-base pairs are formed as expected (Figure 1 a,b). The local helical parameters, intra-base pair parameters and pseudorotation phase angles indicate that these RNA duplexes maintain the standard A-form conformation, regardless of C–Ag^I–C formation (Supporting Information, Tables S3, S4).

The $2|F_o|-|F_c|$ electron density maps and the molecular models of the C–Ag^I–C base pairs show that one Ag^I is placed at the center of a CC mismatch (Figure 1 c; Supporting Information, Figure S2). The distances between the N3 atoms of the C_4 and C_9 residues and Ag^I are 2.2–2.3 Å, indicating that N3 coordinates to Ag^I by using its lone pair. The N3–Ag^I–N3 angles are 177–180°. The linear coordination is very similar to that observed in a previously reported NMR structure of a DNA duplex containing a synthetic metallo-base pair, imidazole–Ag^I–imidazole, in which the Ag^I–N3 distances are 2.1 Å.[12] The propeller twist angles of the C–Ag^I–C base pairs (−29–−27°) are remarkably larger than those of the canonical Watson–Crick base pairs in the A-form RNA duplex (−12°) (Figure 1 d;Supporting Information, Figure S2, Table S3). The propeller twist along the linear N3–Ag^I–N3 bond apparently occurs owing to the repulsion between amino groups at the fourth positions of cytosines. In fact, the N4–N4 distances (4.9–5.1 Å) are longer than the O2–O2 distances (3.9–4.4 Å). The Ag^I does not make any special interaction with the upper and lower base pairs. The distances of C1′–C1′ (9.1–9.6 Å) of the C–Ag^I–C base pairs are about 1 Å shorter than that of the canonical Watson–Crick base pairing (10.7 Å). However, RNA maintains the A-form conformation.

The detailed geometry of the C–Ag^I–C base pair agrees with the previously determined 1:1 binding stoichiometry between Ag^I and the CC mismatch,[9] and is very similar to that of the T–Hg^{II}–T base pair solved by our X-ray analysis, where one Hg^{II} is placed at the center of a TT mismatch and makes linear coordination to two deprotonated N3 atoms of T residues with 2.0 Å distances (Supporting Information, Figure S3 a).[6] On the other hand, the geometry is completely different from a complex between Ag^I and 1-methylcytosine where two Ag^I ions bridge between two 1-methylcytosines in *trans* geometry through O2–Ag^I–N3 coordinate bonds (Supporting Information, Figure S3 b),[13] and also from a complex between Pt^{II} and cytosine where one Pt^{II} ion makes square planer coordination with two cytosines and two ammonias (Supporting Information, Figure S3 c).[14]

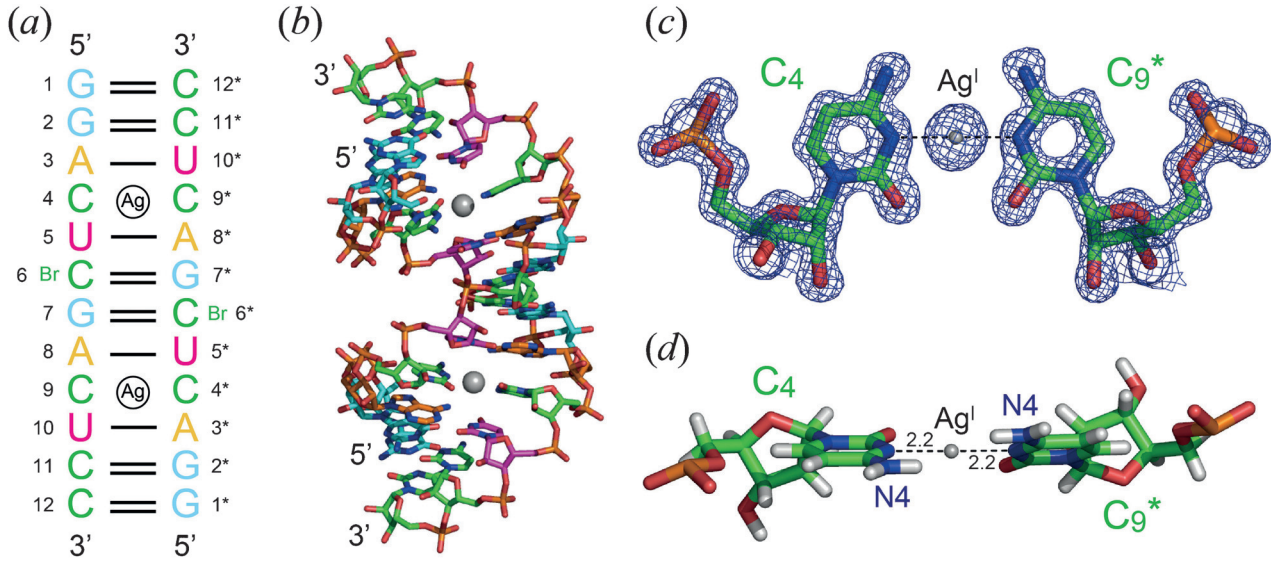

Figure 1. Secondary (a) and crystal structures (b) of the A-form RNA duplex obtained in the presence of Ag^I and local structure of C–Ag^I–C base pair (top view with local $2|F_o|-|F_c|$ (blue: 1.5 σ contour level) map (c), and side view (d). In these figures, Ag^I ions are shown as gray spheres. Coordinate bonds between N3 of C and Ag^I are represented by dashed lines with distances in Å.

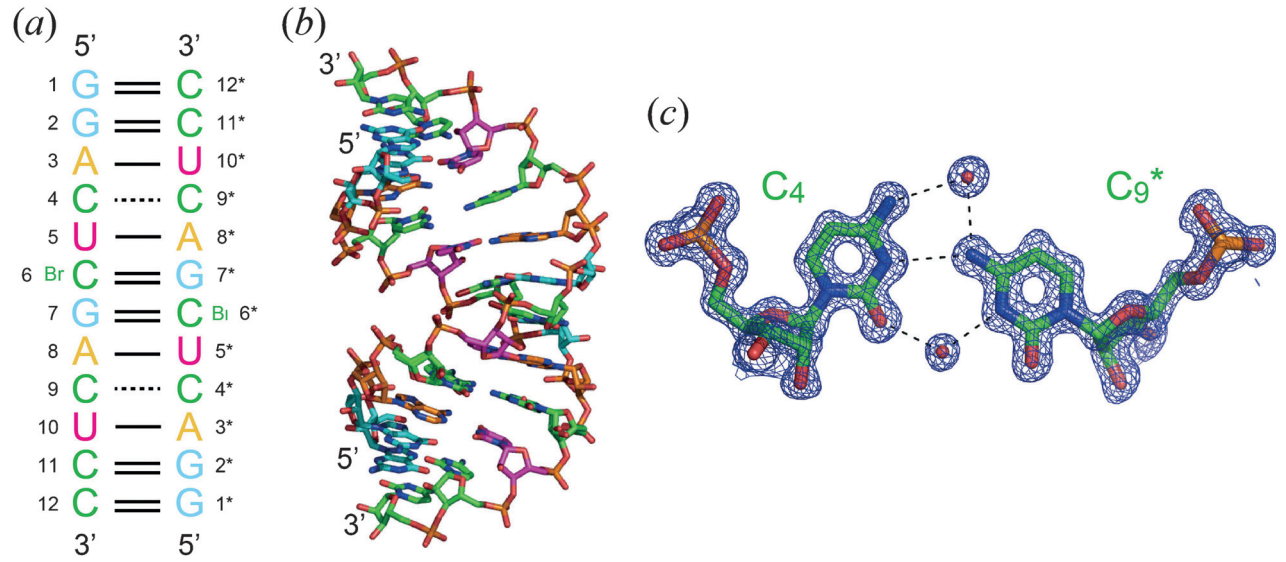

Figure 2. Secondary (a) and crystal structures (b) of the A-form RNA duplex obtained in the absence of Ag^{I} and local structure of water-mediated C–C base pair (top view with local $2|F_o|-|F_c|$ (blue: 1.5 σ contour level) map (c)). Hydrogen bonds are represented by dashed lines.

In the absence of Ag^{I}, RNA-C_4C_9 adopts the A-form double helical structure (Figure 2). The duplex is almost identical to the two duplexes obtained in the presence of Ag^{I} (Supporting Information, Figure S4). In the duplex, two CC mismatches form asymmetrical water-mediated C–C base pairs through one direct hydrogen bond N3(C_4)···H–N4(C_9*), and two water-mediated hydrogen bonds N4(C_4)–H···O···H–N4(C_9*) and O2(C_4)···H–O–H···N3(C_9*) (Figure 2c; Supporting Information, Figure S5). The base pair is different from the *cis* Watson–Crick C–C^+ base pair with O2(C)···H–N3(C^+) and N3(C)···H–N4(C^+) hydrogen bonds (Supporting Information, Figure S3d).[15] In the case of the C_4–C_9* base pair, C_4 stays at its usual position and C_9* shifts toward the minor groove of the RNA duplex, thereby making a well-ordered C_4–C_9* base pair. On the other hand, the C_9–C_4* base pair is disordered between two conformations (Supporting Information, Figure S5b). Since the C1′–C1′ distances of the two water-mediated C–C base pairs (10.7–10.8 Å) are very similar to those of the Watson–Crick base pairs (10.6 Å in average), the RNA duplex is not distorted at all (Supporting Information, Tables S5, S6).

To confirm the Ag^{I}-selectivity of the CC mismatch, we have also determined a structure of the RNA-C_4C_9/Hg^{II} crystal obtained in the presence of Hg^{II}. The RNA-C_4C_9/Hg^{II} crystal is isomorphous with the RNA-C_4C_9 crystal obtained in the absence of Ag^{I} (Supporting Information, Table S2) and RNA duplexes observed in these crystals are identical to each other (Supporting Information, Figure S6). In agreement with our previous result of melting temperature analyses,[8] Hg^{II} did not bind to the CC mismatches in the RNA-C_4C_9 duplex (Supporting Information, Figure S7). Any strong electron density of Hg^{II} was not observed, meaning that Hg^{II} ions may exist in the crystal lattice but their bindings to the RNA duplex are not specific.

In the past decade, several natural[8,9,11,16] and artificial[12,17] Ag^{I}-mediated base pairs have been found and constructed. However, only one detailed tertiary structure, a DNA duplex containing imidazole–Ag^{I}–imidazole base pairs determined by NMR, has been reported so far.[12] In the present study, we have successfully determined high resolution crystal structures of RNA duplexes containing CC mismatches in the presence and absence of Ag^{I} and Hg^{II}. These crystal structures revealed the following: i) Ag^{I} specifically binds to the CC mismatch and forms the C–Ag^{I}–C base pair through N3–Ag^{I}–N3 linear coordination; ii) Ag^{I} does not disturb the standard A-form conformation of RNA by forming the C–Ag^{I}–C base pairs; iii) the C–Ag^{I}–C base pair is structurally similar to the canonical Watson–Crick base pairs as well as T–Hg^{II}–T metallo-base pair, iv) the Ag^{I}-selectivity of the CC mismatch was crystallographically confirmed. Now we have detailed structural information of the two Watson–Crick-like metallo-base pairs T–Hg^{II}–T and C–Ag^{I}–C, which are composed of natural nucleobases and have high metal ion selectivity. This information opens the door to the possibility of structure-based design of nucleic acid-based nanodevices containing the natural metallo-base pairs.

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