Dinuclear Metal-Mediated Homo Base Pairs with Metallophilic Interactions: Theoretical Studies of \( \text{G}_2\text{M}_2^{2+} \) (\( \text{M} = \text{Cu}, \text{Ag}, \text{and Au} \)) Ions

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Dinuclear metal-mediated homo base pairs are interesting clusters with highly symmetric structures and significant stabilities. The geometric and electronic structures of \( \text{G}_2\text{M}_2^{2+} \) (\( \text{G} = \text{Guanine}, \text{M} = \text{Cu}, \text{Ag} \) or \( \text{Au} \)) cluster ions were studied with quantum chemical calculations. The lowest-energy isomers of \( \text{G}_2\text{M}_2^{2+} \) cluster ions have \( \text{C}_{2h} \) symmetries with an approximately antiparallel alignment of two sets of N-M∙∙∙O groups being formed in the planar structures. The M-M distances are shorter than the sum of van der Waals radii of corresponding two homo coinage metal atoms, showing that metallophilic interactions significantly exist in these complexes. They have the large HOMO−LUMO gaps of about 5.80 eV at the DFT level and the bond dissociation energies of more than 5.60 eV at the DFT/B3LYP level, indicating that these cluster dications are highly stable. The second lowest-energy isomers stabilized by an approximately parallel alignment of one set of O-M-O group and one set of N-M-N group are found to be close to the lowest-energy isomers in energy. The barrier between the two isomers of \( \text{G}_2\text{M}_2^{2+} \) cluster ions is significantly large, also showing that these lowest-energy isomers are very stable.

Metal ion-base pair complexes have attracted tremendous attention because of their importance in the development of nanotechnology and biotechnology. They have significantly thermal duplex stabilization as well as the conductive property. It has been reported that metal-mediated base pairs can be used as nanowires, novel sensors competent to detect metal ions in aqueous solutions, bifacial nucleobases, and logic gates. In these metal ion-base pair complexes, dual complementary hydrogen bonds between nucleobases are replaced by the metal-nucleobase bonds. Dinuclear metal ion-mismatched base pairs have become an interesting class of metal ion-base pair complexes in recent years. There have been many theoretical and experimental investigations on the complexes of dinuclear silver ions and mismatched base pairs. More recently, dinuclear CuII and HgII complexes containing an artificial nucleobase (9-ethyl-1, N6-ethenoadenine) have been prepared and their crystal structures have been determined by Mandal et al. Their studies show that dinuclear T-HgII base pair has two sets of parallel M-N bonds with anionic ligands partially compensating the charge of metal ions.

The terms “aurophilic bonding” and “aurophilic interactions” for Au+-Au+ interactions were introduced by Schmidbaur et al. in 1988. The weaker attractive interactions between coinage metal cations with closed-shell configurations in coinage metal compounds have been termed as “numismophilicity” (from the Latin word “numisma” meaning a coin) by Vicente et al. in 1993, and then extended as “metallophilic interactions” for closed-shell interactions of metal atoms by Pyykkö in 1994. Metallophilic interactions are stronger than van der Waals forces but weaker than covalent bonding, close to hydrogen bonding in energy, influencing significantly a number of structural and characteristics of metal compounds. Concerning the intensities of metallophilic interactions, it is generally believed that aurophilic interactions should be stronger than argentophilic bonding due to the strong relativistic effects of Au. Ag ≈ Au seems more reasonable because Ag-Ag distances are very close to Au-Au distances in a family of analogous complexes.

In our preceding papers, we have investigated the coinage metal-nucleobase complexes by photoelectron spectroscopy, photodissociation, and theoretical calculations. \( \text{G}_2\text{M}^+ \) (\( \text{G} = \text{guanine}, \text{M} = \text{Cu}, \text{Ag} \) or \( \text{Au} \)) cluster ions prefer planar structures with the metal cations interacting with the N7 atoms of guanine. In my previous papers, metal-to-ligand (MLCT), ligand-to-metal (LMCT), intraligand (LL) charge transfer processes have been
found to exist in the photodissociation of G2M2+ ions. The bonding and electronic structures of dinuclear coinage metal-mediated base pairs containing divalent metal ions remain elusive. Cu2+, Ag2+, and Au2+ cations have a 1S electronic ground state with the valence electron configuration nd10(n + 1)s0(n + 1)p0. This poses the question about the electron configuration of metal cations in G2M2+ complexes and the nature of chemical bonding in the metallophilic and nucleobase-M2+-nucleobase interactions. Gold exhibits larger relativistic effects than those of Cu and Ag, such as 5d relativistic expansion and destabilization, and 6s relativistic stabilization and contraction32–39. It is interesting to pinpoint whether dinuclear coinage metal-mediated homo base pairs are also stable and in which direction gold-mediated base pairs might deviate from the copper or silver analogues. In this work, we investigate the whole G2M2+ series for M = Cu, Ag and Au and examine the chemical bonding using various theoretical methods. The calculated results for the G2M2+ complexes provide new aspects for chemical bonding of the coinage metals and help to find potential applications of metal-mediated base pairs complexes.

Theoretical results

In search of the global minimum of G2M2+ (M = Cu, Ag or Au) cluster dications, various possible initial geometric structures have been considered. The canonical (K-N9H) tautomer40 of guanine was taken into account in the search of their low-energy isomers. The structures, bond lengths, and N-M-O angles of low-energy isomers of these complexes are displayed in Fig. 1 and Table 1. Relative energies (eV), symmetries and electronic states of the low-energy isomers of G2M2+ cluster ions are shown in Table 2. The optimized structures of G2M2+ cluster ions are in singlet spin states. The triplet and quintet spin states are much less stable than the singlet spin states in energy. All of these complexes are planar structures in guanine-M2-guanine style, containing one set of nearly linear N–M–N and one group of roughly linear N–M–O bonds.

As seen in Fig. 1, all the lowest-energy isomers 1A, 2A and 3A of G2M2+ cations have perfectly planar structures with C2h symmetries. An approximately antiparallel orientation of two sets of N–M–O groups are formed in these isomers 1A, 2A and 3A. The N–M–O units have nearly linear arrangements and the order of their angles is Cu < Au < Ag (∠N-Cu-O = 168.7°, ∠N-Ag-O = 174.1°, ∠N-Au-O = 173.1°). The Cu-N distances are near 1.893 ± 0.010 Å, and Cu-O distances are 1.855 ± 0.006 Å, depending on the structures. The order of M-N or M-O distances is Cu < Au < Ag, in agreement with the order of the atomic radii increments suggested by Pyykkö41 (Cu ~ 1.12 Å, Ag ~ 1.28 Å, Au ~ 1.24 Å). Considering the Au-Au distances, aurophilic Au-Au distances can vary from 2.85 Å to 3.50 Å depending on their strength28. The Au-Au distance is 2.991 Å in the lowest-energy isomer 3A, much larger than the single-bond covalent radii (2.48 Å) recommended by Pyykkö41, indicating that there is hardly strong Au–Au bonding interaction except the aurophilic interaction. The Ag-Ag distance is near 2.982 Å in isomer 2A, significantly longer than the distance of a Ag–Ag single bond (2.53 Å), but shorter than the sum of van der Waals radii (3.44 Å)32. It is very close to the Au-Au distance in isomer 3A, showing that the

Figure 1. Structures and relative energies of the low-lying isomers of G2M2+ cluster ions. The bond distances are in angstroms.
Table 1. Optimized Bond Lengths and ∠N-M-O Angles of the Lowest-lying Isomers of G2M22+ Cluster Ions at the DFT Levela. The bond distances are in angstroms and the bond angles are in degrees.

| Cluster Ions | Symm. | State | ∠N-M-O (deg) | ∠N-Cu-O (deg) |
|--------------|-------|-------|--------------|---------------|
| Cu-Cu        | C2v   | 1A    | 182.1        | 167.5         |
| Cu-N         | C2v   | 1A    | 172.0        | 167.5         |
| Cu-O         | C2v   | 1A    | 176.8        | 167.5         |
| Ag-Ag        | C2v   | 1A    | 180.0        | 167.5         |
| Ag-N         | C2v   | 1A    | 170.0        | 167.5         |
| Ag-O         | C2v   | 1A    | 176.8        | 167.5         |

Table 2. Relative Energies (eV), Symmetries and Electronic States of the Low-energy Isomers of G2M22+ Cluster Ions.

| Isomers | Symm. | State | PBE/TZ2P | CAMY-B3LYP | COSMO |
|---------|-------|-------|----------|------------|-------|
| 1A      | C2v   | 1A    | 0.00     | 0.00       | 0.00  |
| 1B      | C2v   | 1A    | 0.00     | 0.00       | 0.00  |
| 1C      | C2v   | 1A    | 0.00     | 0.00       | 0.00  |
| 2A      | C2v   | 1A    | 0.00     | 0.00       | 0.00  |
| 2B      | C2v   | 1A    | 0.00     | 0.00       | 0.00  |
| 2C      | C2v   | 1A    | 0.00     | 0.00       | 0.00  |
| 3A      | C2v   | 1A    | 0.00     | 0.00       | 0.00  |
| 3B      | C2v   | 1A    | 0.00     | 0.00       | 0.00  |
| 3C      | C2v   | 1A    | 0.00     | 0.00       | 0.00  |

metallophilic bonding for Ag and Au is very similar. The Cu-Cu distances in isomer 1A are near 2.797 Å, close to the distances of the dimer [H3PAgCl] with cuprophilic interactions (2.637–2.809 Å at DFT and ab initio levels)52. Concerning metal–metal vibrations, the Cu–Cu vibrational harmonic frequency of isomer 1A is 122.5 cm⁻¹ (force constant F = 0.33 mdyn•Å⁻¹). The Ag–Ag vibrational frequency of isomer 2A is 101.1 cm⁻¹ (force constant F = 0.47 mdyn•Å⁻¹), in accordance with the Ag–Ag vibrations (75–125 cm⁻¹) of crystals of Tl[Ag(CN)₂] detected by a detailed Raman experiment40. The Au–Au vibrational frequency of isomer 3A is 94.8 cm⁻¹ (force constant F = 0.57 mdyn•Å⁻¹). The order of M–M stretching frequencies is Cu > Ag > Au.

The second lowest-energy isomers 1B, 2B, and 3B of G2M22+ cluster ions can be considered as derived from isomers 1A, 2A, and 3A, respectively, by revolving guanine about 180° round the C2 axis. They are stabilized by an approximately parallel orientation of one set of O–M–O group and one set of N–M–N group, close to the lowest-lying isomers in energy at the DFT level. One note that isomer 3B has a nonplanar structure with C3 symmetry. The M–M distances in isomers 1B–3B are slightly shorter than those in isomer 1A–3A. The third lowest-energy isomers of G2M22+ cluster ions have planar structures with one metal ion involving in the formation of one set of O–M–O group and another metal ion binding to N7 atom of guanine. Isomers 1C, 2C, and 3C are much higher in energy than the lowest-lying isomers 1A, 2A, and 3A. When the aqueous solvent environment is roughly modeled using the COSMO solvent model, the energy differences of two lowest-energy isomers become closer relative to those in the vacuum environment. All the bond lengths become slightly shorter and the order of ∠N–M–O angles becomes Cu < Ag < Au.

Effective atomic charges of the lowest-energy isomers (1A, 2A, and 3A) of G2M22+ (M = Cu, Ag, and Au) cluster ions from various population schemes are displayed in Table 3. The charges from the multipole-deformation prescription are slightly larger than those from the Hirshfeld or Voronoi Deformation Density (VDD) prescriptions. Our studies have shown that the Voronoi and Hirshfeld density partitionings are consistent with the chemical shifts of the core-level energies of atoms44. According to the Hirshfeld or VDD prescriptions, the coinage metals Cu, Ag, and Au carry large positive charges between 0.18 and 0.34, while the nitrogen and oxygen atoms bonded to the metal atoms carry negatively charges. Thus, strong electrostatic attraction exist in the interactions between the metal atoms and N or O atoms, while the electron-acceptor strength of coinage metal atoms has the order Au > Cu > Ag.

To understand the relative stabilities of the lowest-lying isomers and the second lowest-energy isomers of G2M22+ cluster ions, the possible transition barriers were calculated between them using the Berny method at the DFT/B3LYP level. Obtained transition-state structures were confirmed to connect the correct reactants and products.
The characters and bonding of the highest occupied 5b\textsubscript{g} MO of G\textsubscript{2}Ag\textsubscript{2} are little stabilized by two sets of 5ag and 6ag MOs.

In three sets of 2ag, 3ag, and 3bu MOs. Seven sets of 3b\textsubscript{g}, 3au, 1bg, 2bu, 1au, 1ag, and 1bu MOs are the combinations of the 3d orbitals of two Cu atoms and the 2p orbitals of C, N, and O atoms. From these analyses, the cuprophilic interaction occurs mainly through the mutual stabilization of nine sets of 3au, 4ag, 2bg, 4bu, 3ag, 3bu, 2au, 2ag, and 3bu MOs, while the 4p orbital of Cu just has 5% contribution to the LUMO. The 3d orbitals of Ag atoms have 97% contribution to the HOMO 5bg (−11.4 eV), while the 3d orbitals of Ag atoms just have 3% contribution to the HOMO. The characters and bonding of the highest occupied 5bu MO of Ag’s lighter homologue. Seven sets of 3ag, 5a\textsubscript{u}, 1a\textsubscript{g}, and 1a\textsubscript{u} MOs have major contribution from N 2p character and minor contribution from the 4d orbitals of Ag atoms, 2p orbitals of C and O atoms, while six sets of 1b\textsubscript{u}, 3a\textsubscript{g}, 2b\textsubscript{u}, 4a\textsubscript{g}, 3b\textsubscript{u}, and 2a\textsubscript{g} MOs have significant contribution from the 4d orbitals of Ag atoms and only little contribution from 2p orbitals of C, N and O atoms. The argentophilic interaction occurs mainly through the mutual stabilization of three sets of low 1b\textsubscript{u}, 2a\textsubscript{g} and 2a\textsubscript{u} MOs, two sets of nearly degenerate 3b\textsubscript{u} and 2b\textsubscript{u} MOs, and two sets of 4a\textsubscript{u} and 4b\textsubscript{u} MOs, and also a little stabilized by two sets of 5a\textsubscript{g} and 6a\textsubscript{g} MOs.

Table 3. Effective Atomic Charges of the Lowest-energy Isomer (1 A, 2 A, and 3 A) of G\textsubscript{2}M\textsuperscript{2+} Cluster Ions.

| M       | Hirshfeld charge | Voronoi charge | MDC-q |
|---------|-----------------|----------------|--------|
| Cu\textsubscript{1}, Cu\textsubscript{2} | 0.29            | 0.27           | 0.39   |
| N1, N2  | −0.11           | −0.13          | −0.40  |
| O1, O2  | −0.21           | −0.22          | −0.42  |
| Ag\textsubscript{1}, Ag\textsubscript{2} | 0.34            | 0.30           | 0.53   |
| N1, N2  | −0.11           | −0.13          | −0.50  |
| O1, O2  | −0.23           | −0.23          | −0.49  |
| Au\textsubscript{1}, Au\textsubscript{2} | 0.22            | 0.18           | 0.43   |
| N1, N2  | −0.08           | −0.09          | −0.50  |
| O1, O2  | −0.20           | −0.19          | −0.48  |

Table 4. Characters, Orbital Energies (in eV), and AO Contributions in % (Largest is Bold) of the Cu 3d-derived MOs and Lowest Unoccupied MO of the Lowest-lying Isomer of G\textsubscript{2}Cu\textsuperscript{2+} dication.

Discussion

The Cu 3d-derived valence MOs and lowest unoccupied molecular orbital (LUMO) 4a\textsubscript{u} of the lowest-energy isomer of G\textsubscript{2}Cu\textsuperscript{2+} cation are displayed in Figure S1 and Table 4. The LUMO 4a\textsubscript{u} has 95% contribution from the 4d orbitals of Ag atoms, 2p orbitals of C, N and O atoms. The argentophilic interaction occurs mainly through the mutual stabilization of three sets of low 1b\textsubscript{u}, 2a\textsubscript{g} and 2a\textsubscript{u} MOs, two sets of nearly degenerate 3b\textsubscript{u} and 2b\textsubscript{u} MOs, and two sets of 4a\textsubscript{u} and 4b\textsubscript{u} MOs, and also a little stabilized by two sets of 5a\textsubscript{g} and 6a\textsubscript{g} MOs.
The $G_2Au_2^{2+}$ cluster ion has 10 Au 5d AOs, which span a$_1$ (1a$_g$, 2a$_g$, 3a$_g$, and 4a$_g$ MOs) + a$_u$ (low 1a$_u$, 2a$_u$, and 3a$_u$ MOs) + 2b$_g$ (1b$_g$ and the highest occupied 2b$_g$ MOs) representations in the C$_2h$ symmetry (Figure S3 and Table 6). Suppressing the Au(5d) AO participation, one note that the lowest unoccupied 4a$_u$ MO at $-5.7$ eV is the combinations of three sets of C(2p), N(2p), O(2p) AOs, and one set of virtual Au(6p) AOs. Mixing of 5d AOs of two gold atoms yields the 2a$_u$ ($-13.4$ eV) $\sigma$ bonding orbitals in the middle of the valence band. Due to the relativistic effects, the strong mixing of Au 5d and 6s AOs in particular the 2a$_g$ ($-14.0$ eV), 4a$_g$ ($-13.0$ eV), and 2b$_u$ ($-11.6$ eV) MOs leads to the significant Au 5d-6s hybridization. It is clear that Au 5d AOs play some role in the highest occupied 2b$_g$ ($-11.5$ eV) MO as the Au 5d AOs and $\pi$g bonding orbital of C(2p), N(2p), and O(2p) AOs counteract each other. From these analyses, the aurophilic interaction occurs mainly through the mutual stabilization of three sets of 5a$_g$, 6a$_g$, and 3b$_u$ $\delta$ orbitals, two sets of 3a$_g$ and 3a$_u$ $\sigma$ orbitals, and

| MO   | $\varepsilon$ | occ | Ag(d) | Ag(s) | Ag(p) | N(p) | O(p) | C(p) | H(s) |
|------|---------------|-----|-------|-------|-------|------|------|------|------|
| 1a$_g$ | $-15.9$ | 2  | 18    | 2     | 54    | 11   | 15   |
| 1a$_u$ | $-14.4$ | 2  | 37    | 1     | 48    | 5    | 10   |
| 1b$_g$ | $-14.5$ | 2  | 72    | 5     | 5     | 21   |
| 1b$_u$ | $-14.4$ | 2  | 27    | 50    | 4     | 19   |
| 2a$_g$ | $-14.3$ | 2  | 94    | 4     | 2     |      |
| 2a$_u$ | $-14.0$ | 2  | 47    | 8     | 40    |
| 2b$_g$ | $-13.9$ | 2  | 53    | 26    | 9     | 12   |
| 2b$_u$ | $-13.6$ | 2  | 30    | 32    |      |      |
| 3a$_g$ | $-13.6$ | 2  | 100   | 1     |      |
| 3a$_u$ | $-13.6$ | 2  | 98    | 2     |      |
| 4a$_g$ | $-13.4$ | 2  | 77    | 3     | 19    |
| 4a$_u$ | $-13.3$ | 2  | 43    | 18    | 37    |
| 5a$_g$ | $-13.0$ | 2  | 32    | 44    |
| 5a$_u$ | $-12.9$ | 2  | 31    | 36    | 26    |
| 4b$_g$ | $-12.9$ | 2  | 20    | 61    | 17    |
| 6a$_g$ | $-12.7$ | 2  | 26    | 14    | 45    | 6    | 9    |
| 4b$_u$ | $-12.0$ | 2  | 65    | 10    | 14    | 9    |
| 3a$_g$ | $-11.4$ | 2  | 3    | 50    | 10    | 37   |
| 3a$_u$ | $-5.4$   | 2  |      | 5     | 25    | 12   | 58   |

Table 5. Characters, Orbital Energies (in eV), and AO Contributions in % (Largest is Bold) of the Ag 4d-derived MOs and Lowest Unoccupied MO of the Lowest-lying Isomer of $G_2Ag_2^{2+}$ Cluster ion.

| MO | $\varepsilon$ | occ | Au(d) | Au(s) | Au(p) | N(p) | O(p) | C(p) | H(s) |
|----|---------------|-----|-------|-------|-------|------|------|------|------|
| 1b$_g$ | $-16.9$ | 2  | 10    | 2     | 57    | 8    | 16   | 7    |
| 1a$_g$ | $-16.6$ | 2  | 11    | 2     | 50    | 13   | 21   | 3    |
| 1a$_u$ | $-15.0$ | 2  | 34    | 50    |      |
| 1b$_g$ | $-14.7$ | 2  | 13    | 61    | 6     |
| 2b$_g$ | $-14.6$ | 2  | 50    | 8     | 39    | 3    |
| 2a$_g$ | $-14.4$ | 2  | 33    | 7     | 60    |      |
| 3a$_g$ | $-14.0$ | 2  | 80    | 20    |      |      |
| 2b$_u$ | $-14.0$ | 2  | 36    | 41    | 14    | 9    |
| 2a$_u$ | $-13.8$ | 2  | 11    | 43    | 2     |
| 3a$_g$ | $-13.4$ | 2  | 100   |      |
| 4a$_g$ | $-13.1$ | 2  | 30    | 57    | 7     |
| 5a$_g$ | $-13.0$ | 2  | 81    | 19    |      |
| 3b$_g$ | $-12.8$ | 2  | 94    | 6     |      |
| 3b$_u$ | $-12.8$ | 2  | 64    | 29    | 4     | 3    |
| 4b$_u$ | $-12.8$ | 2  | 73    | 21    | 5     | 1    |
| 6a$_g$ | $-12.7$ | 2  | 57    | 10    | 6     | 2    |
| 4a$_u$ | $-12.6$ | 2  | 59    | 18    | 16    | 7    |
| 4b$_u$ | $-11.6$ | 2  | 57    | 3     | 7     |
| 5b$_g$ | $-11.5$ | 2  | 10    | 45    | 10    | 35   |
| 5a$_u$ | $-5.7$  | 2  |      | 3     | 26    | 13   | 58   |

Table 6. Characters, Orbital Energies (in eV), and AO Contributions in % (Largest is Bold) of the Au 5d-derived MOs and Lowest Unoccupied MO of the Lowest-lying Isomer of $G_2Au_2^{2+}$ Cluster ion.
also a little stabilized by three sets of 4b_u, 4a_u and 2b_u MOs, and two sets of degenerate 3b_g and 4b_g MOs. It is worth mentioning that, the bonding interaction in Au_2G_2^2+ cluster ion involves the valence electron configuration 5d⁹6s¹6p⁰ rather than the nd⁴(n + 1)s⁰(n + 1)p⁰ configuration at Cu or Ag in Au's homologues. The result seems reasonable because the relativistic effects in the valence shells of gold atom stabilize the s-atomic orbitals (AOs) and destabilize the d-AOs, leading to the drastically reduced 5d-6s gap of Au, and then resulting in Au's particular electron configuration in the metal-mediated base pairs complexes.

For G_2Cu_2^2+ cluster dication, the HOMO (Cu d) → LUMO (G_2 π) excitation can be classified as metal-metal-to-ligand charge transfer (MMLCT), while for G_2Ag_2^2+ and G_2Au_2^2+ cluster dications, the HOMO → LUMO excitations are able to be classified as ligand-to-ligand (LL) charge transfer. These charge transfer processes are different from those in mononuclear metal-mediated base pairs, modified significantly by the presence of the Cu–Cu, Ag–Ag, and Au–Au interactions. It may provide valuable information for their absorption or photodissociation experiments.

The lowest-energy isomer 2A of G_2Ag_2^2+ dication has larger HOMO – LUMO gap of 5.98 eV at the DFT level, as compared to Ag's heavier (HOMO-LUMO gap nearly 5.80 eV) and lighter homologue (HOMO-LUMO gap nearly 5.58 eV). However, the bond dissociation energies (BDEs) of G_2M_2^2+ cluster ions calculated based on the differences between the total energy of the parent ion (G_2M_2^2+) and the total energies of all the fragments (G and M+) at the DFF/B3LYP level (G_2M_2^2+ → 2 G + 2 M+) are 8.52, 5.66, 8.50 eV, for Cu, Ag, and Au, respectively. This indicates that the sum of N-M, M-O, and metallophilic interactions in G_2Ag_2^2+ cluster ion is much weaker than those in Ag's heavier and lighter homologues.

Because dinuclear metal-mediated base pairs can be introduced as DNA sequences, it is interesting to compare the structural parameters of isolated G_2M_2^2+ cluster ions with those of TGM_2GT^2+ (M = Cu, Ag and Au) cluster ions. Structures and M-N, M-O and M-M bond lengths of optimized TGM_2GT^2+ (M = Cu, Ag and Au) cluster ions have been shown in Fig. 2. The Cu-N and Cu-Cu bond lengths of TGCu_2GT^2+ ions have been slightly shortened relative to those of G_2Cu_2^2+ cluster ions, while the Ag-N bond lengths of TGAu_2GT^2+ ion are slightly shorter than those of G_2Ag_2^2+ ions. TGAu_2GT^2+ ion has slightly longer Au-Au bond length when compared with G_2Au_2^2+ ions. Lengthened sequences containing G_2Cu_2^2+ and G_2Au_2^2+ cluster ions have slightly weaker
metallophilic interactions relative to the isolated $G_2M_2^{2+}$ cluster ions. However, lengthened sequences containing $G_2Ag_2^{2+}$ cluster ions have almost the same argentophilic interactions relative to the isolated $G_2M_2^{2+}$ cluster ions.

**Conclusions**

The geometric and electronic structures of $G_2M_2^{2+}$ ($G = Guanine, M = Cu, Ag or Au$) cluster ions have been investigated with DFT approaches. The lowest-lying isomers of the presently investigated species have $C_{2v}$ symmetries with an approximately antiparallel alignment of N-M-O groups being formed in the planar structures. Their HOMO-LUMO gaps significantly above 5.50 eV at the DFT level, indicating that these cluster dications are highly stable. The Ag-Ag, and Au-Au distances in these isomers are very similar, slightly longer than the Cu-Cu distance. Cu-Cu, Ag-Ag and Au-Au distances are shorter than the sum of van der Waals radii of corresponding two homo coinage-metal atoms, showing that metal-metal bonding can be characterized as weak but significant metallophilic interactions. From above-mentioned orbital analyses, s and d orbitals of metal atoms and p orbitals of C, N and O atoms all significantly participate in the orbital interactions. The compositions and bonding of the HOMO of $G_2Cu_2^{2+}$ dication are completely different from those of the highest occupied MOs of Cu's heavier homologues. The bonding interactions in $Au_2G_2^{2+}$ dication involve the valence electron configuration $5d^96s^6p^6$ rather than the nd$^{10}$(n+1)$s^8(n+1)p^6$ configuration at Cu or Ag in Au's homologues, although it may not be attached as an absolute physical meaning. The second lowest-energy isomers stabilized by an approximately parallel alignment of one set of O-M-O group and one set of N-M-N group are found to be close to the lowest-energy isomers in energy. The barrier between the two isomers of $G_2M_2^{2+}$ cluster ions is significantly large, also showing that these lowest-energy isomers are very stable.

**Theoretical methods**

To investigate the geometric structures and energetics of $G_2M_2^{2+}$ ($G = guanine, M = Cu, Ag or Au$) cluster dications, DFT calculations were performed with Amsterdam Density Functional program (ADF 2013.01)\textsuperscript{43–47}. The geometries were fully optimized using the generalized gradient approximation (GGA)\textsuperscript{49} of Perdew–Becke–Ernzerhof (PBE), converging to an energy gradient $< 10^{-5}$ Hartree–nt Å\textsuperscript{-1} at an Kohn–Sham SCF criterion $< 10^{-6}$ a.u. The uncontracted Slater basis sets with the quality of triple-plus two polarization functions (TZ2P) were used, with the frozen core approximation applied to the [1s 2-4f14] core for Au, [1s 1] core for H and the [1s 2] cores for C, N and O. The scalar relativistic was taken into account by the Zero Order Regular Approximation (ZORA). Optimized minimum structures were verified with nonexistence of imaginary frequencies in the analyses of vibrational frequencies. For more reliable energies, the single-point energy was calculated using the CAMY-B3LYP/TZ2P\textsuperscript{49} density functional method at the PBE/TZ2P geometries. The corrections of zero-point energy (ZPE) were also included in calculating the relative energies. To determine the atomic charges of Cu, Ag, Au, relevant N, and O atoms in these clusters, the population partitioning schemes of Hirshfeld\textsuperscript{90,91}, Voronoi\textsuperscript{92}, and multipole derived charges (MDC-q)\textsuperscript{93} were calculated.

The conductor-like screening model (COSMO) was also used to approximately explore the influence of a aqueous solvent environment on the geometries and energetics of the $G_2M_2^{2+}$ cluster cations\textsuperscript{94}. The following atomic COSMO-default radii from the ADF code were used: H 1.350, C 1.700, N 1.608, O 1.517, Cu 1.883, Ag 2.025, and Au 2.025\textsuperscript{95}. The parameters for water solvent were used in the COSMO calculations as water was the most common solvent used in the experimental studies for comparison.

The structures of $G_2M_2^{2+}$ ions and transition states between two nearly degenerated isomers of $G_2M_2^{2+}$ cluster dications were optimized using the GAUSSIAN 09 program\textsuperscript{96}. The Becke 3-parameter-Lee–Yang–Parr (B3LYP)\textsuperscript{97,98} density functional method with the 6–31 + $+$ G(d,p) basis set was chosen for nucleobases. The ECP10MDF, ECP28MDF, ECP60MDF relativistic effective core potential (RECP) developed by the Stuttgart–Cologne groups were chosen for Cu 1s-2p (3spd4s), Ag 1s-3d (4spd5s), and Au 1s-4f (5spd6s), respectively\textsuperscript{99}. Gaussian type one-electron basis sets of MDF-VDZ were used for Cu, Ag and Au\textsuperscript{100,101}.

**References**

1. Clever, G. H. & Shionoya, M. Metal–base pairing in DNA. *Coord. Chem. Rev*. **254**, 2391–2402 (2010).
2. Mas-Ballesté, R. et al. Towards Molecular Wires Based on Metal-Organic Frameworks. *Eur. J. Inorg. Chem.* **2009**, 2885–2896 (2009).
3. Liu, J., Cao, Z. & Lu, Y. Functional nucleic acid sensors. *Chem. Rev.* **109**, 1948–1998 (2009).
4. Mueller, J. Metal-ion-mediated base pairs in nucleic acids. *Eur. J. Inorg. Chem.* **2008**, 3749–3763 (2008).
5. Tanaka, K. & Shionoya, M. Programmable metal assembly on bio-inspired templates. *Coord. Chem. Rev.* **251**, 2732–2742 (2007).
6. He, W., Franzini, R. M. & Achim, C. Metal-Containing Nucleic Acid Structures Based on Synergetic Hydrogen and Coordination Bonding. *Prog. Inorg. Chem.* **55**, 345–612 (2007).
7. Clever, G. H., Kaul, C. & Carell, T. DNA-metal base pairs. *Angew. Chem. Int. Ed.* **46**, 6226–6236 (2007).
8. Ono, A., Torigoe, H., Tanaka, Y. & Okamoto, I. Binding of metal ions by pyrimidine base pairs in DNA duplexes. *Chem. Soc. Rev.* **40**, 5855–5866 (2011).
9. Ono, A. & Togashi, H. Highly selective oligonucleotide-based sensor for mercury (II) in aqueous solutions. *Angew. Chem. Int. Ed.* **43**, 4300–4302 (2004).
10. Takezawa, Y., Nishiyama, K., Mashima, T., Katahira, M. & Shionoya, M. Bifacial Base-Pairing Behaviors of 5- Hydroxyuracil DNA Bases through Hydrogen and Metal Coordination. *Chem.-Eur. J.* **21**, 14713–14716 (2015).
11. Carell, T. Molecular computing: DNA as a logic operator. *Nature* **469**, 45–46 (2011).
12. Santanam, D., Diaz, N., Mendoza-Arriaga, J. M., Salas, J. M. & Galindo, M. A. Highly Stable Double-Stranded DNA Containing Sequential Silver (I)-Mediated 7-Deazaadenine/Thymine Watson–Crick Base Pairs. *Angew. Chem. Int. Ed.* **55**, 6170–6174 (2016).
13. Okamoto, I., Iwamoto, K., Watanabe, Y., Miyake, Y. & Ono, A. Metal-Ion Selectivity of Chemically Modified Uracil Pairs in DNA Duplexes. *Angew. Chem. Int. Ed.* **48**, 1648–1651 (2009).
14. Okamoto, I., Ono, T., Sameshima, R. & Ono, A. Metal ion-binding properties of DNA duplexes containing thioimadazole base pairs. *Chem. Commun.* **48**, 4347–4349 (2012).
15. Megger, D. A. et al. Contiguous Metal-Mediated Base Pairs Comprising Two Ag Ions. *Chem.-Eur. J.* **17**, 6533–6544 (2011).
16. Yang, H., Mei, H. & Seela, F. Pyrrolo-dC Metal-Mediated Base Pairs in the Reverse Watson–Crick Double Helix: Enhanced Stability of Parallel DNA and Impact of 6-Pyridinyl Residues on Fluorescence and Silver-Ion Binding. *Chem.-Eur. J.* **21**, 10207–10219 (2015).
17. Jana, S. K., Guo, X., Mei, H. & Seela, F. Robust silver-mediated imidazolono-dC-base pairs in metal DNA: Dinuclear silver bridges with exceptional stability in double helices with parallel and antiparallel strand orientation. Chem. Commun. 51, 17301–17304 (2015).
18. Mei, H., Ingale, S. A. & Seela, F. Imidazolono-dC-Metal-Mediated Base Pairs: Purine Nucleosides Capture Two Ag⁺ Ions and Form a Duplex with the Stability of a Covalent DNA Cross-Link, Chem. Eur. J. 20, 16248–16257 (2014).
19. Mei, H., Röhl, I. & Seela, F. Ag⁺-mediated DNA base pairing: extraordinarily stable pyrrolo-dC-pyrrolo-dC pairs binding two silver ions. J. Org. Chem. 78, 9457–9463 (2013).

Mandal, S., Hepp, A. & Müller, J. Unprecedented dinuclear silver (I)-mediated base pair involving the DNA lesion 1, N6-ethenoadenine. Dalton Trans. 44, 3540–3543 (2015).

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Author Contributions
G.-J.C. conceived the idea, performed the calculations and wrote the manuscript.
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