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Alternate Arrangements of Two Different Metals at Chemically-Equivalent Binding Sites on a Circle

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A regular array of metal ions formed using predesigned template ligands is a general, widely applicable strategy for constructing discrete or infinite multinuclear metal complexes that offer metal-ion-dependent and array-structure-based features.[1] To achieve precise arrangement of a few kinds of metal ions in a programmable way, much effort has been devoted to designing metal ligands in such a way that each binding site has a different binding affinity to a specific metal ion.[2] In this context, we recently reported that linear two-coordinate Ag^+ and Hg^{2+} ions can be hierarchically arranged on a 2D plane of disk-shaped ligand **1** possessing six oxazoline rings, three of which are on the inner $\mathbf{G}^1$ site and the others on $\mathbf{G}^2$ sites (Figure 1). In the thermodynamically stable sandwich-shaped $[Ag_3Hg_3\mathbf{1}_2]^{9+}$ complex, three Ag^+ and three Hg^{2+} ions are arranged on the $\mathbf{G}^1$ and $\mathbf{G}^2$ sites, respectively.[2d] This site-selective heterologous metal arrangement was best explained by the minimization of the Coulombic repulsion between the adjacent positively charged metal centers. The severity of the electrostatic force between two point charges depends mainly on their valence and distance. For instance, it is hard to arrange three divalent Hg^{2+} ions on the three 5.9 Å-spaced $\mathbf{G}^1$ sites on a circle because of the Coulombic repulsion that should take place between the Hg^{2+} ions, in spite of the fact that Hg^{2+} ions have a larger affinity to the nitrogen donors. As a result, three monovalent Ag^+ ions can be specifically arranged on the $\mathbf{G}^1$ sites with a higher stability. On the other hand, Hg^{2+} ions form a more stable complex than Ag^+ ions on the three 13.4 Å-spaced $\mathbf{G}^2$ sites, as the Coulombic repulsion is no longer a predominant factor determining the thermodynamic stability. Thus, Ag^+ and Hg^{2+} ions are hierarchically placed on the $\mathbf{G}^1$ and $\mathbf{G}^2$ sites, respectively, despite the fact that all of the binding sites on the two circles are chemically equivalent.

In order to further understand and develop a methodology for electrostatically controlled arrangement of two different metal ions on a circle, we have designed the novel disk-shaped hexamonodentate ligands **2** and **3**, each having a sixfold axis (Figure 1). Since these ligands have six chemically equivalent oxazoline rings on the 7.8 Å-spaced $\mathbf{G}^2$ sites, when a mixture of monovalent and divalent metals is used for complexation, both the $M^{n+}-N$ bond strength and the degree of Coulombic interactions would be considered as factors that determine the thermodynamically favorable products. Accordingly, for instance, a mixture of monovalent and divalent metal ions was expected to be regularly arrayed by ligand **2** or **3** with well-balanced intramolecular Coulombic interactions and coordination stabilization. In this study, we found that three monovalent M^+ (M = Ag, Cu) and three divalent Hg^{2+} ions are alternately arranged on a circle with a diameter of 1.5 nm in such a way that the six metal ions are placed between two template disk-shaped hexamonodentate ligands **2** (Figure 1).

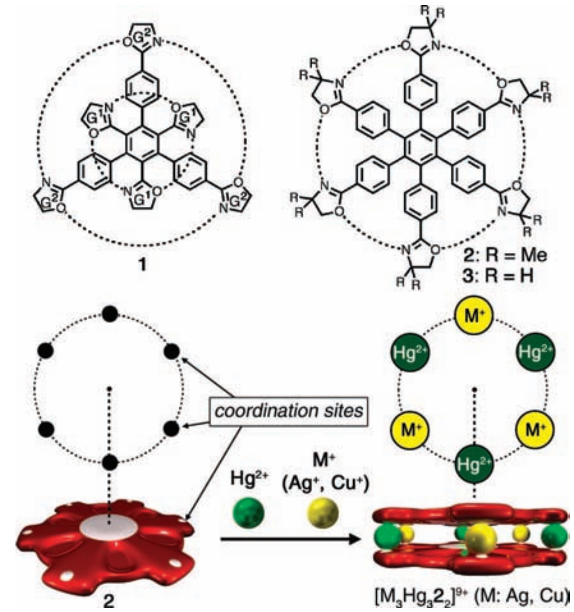

Figure 1. Schematic representation of the alternate arrangement of M^+ (M = Ag, Cu) and Hg^{2+} ions to form sandwich-shaped hexanuclear complexes $[M_3Hg_3\mathbf{2}_2]^{9+}$.

Prior to an examination of how two kinds of d^{10} transition-metal ions such as Ag^+, Cu^+, and Hg^{2+} are arranged on ligand **2**, complexation of the individual metal ions was studied.[3] As a result, the sandwich-shaped hexanuclear complexes $[M_6\mathbf{2}_2]^{6n+}$ (M^{n+} = Ag^+, Cu^+, Hg^{2+}) were quantitatively formed from **2** and the metal ions in 1:1 $CD_3OD/CDCl_3$.[4] ^1H NMR spectra of these complexes showed four resonances assigned to the *p*-phenylene protons H^b and H^c, indicating that the inner and outer protons are inequivalent as a result of the formation of a sandwich-shaped structure (Figure 2b−d).[5] The solution structures of the $[M_6\mathbf{2}_2]^{6n+}$ complexes were revealed by electrospray ionization time-of-flight (ESI-TOF) mass spectrometry (Figures S1−S3 in the Supporting Information).

In contrast, when two kinds of metal ions with different charges, Ag^+/Cu^+ and Hg^{2+}, were used, the ions were found to be alternately arranged on a circle upon complexation with **2** in 1:1 $CD_3OD/CDCl_3$. The ^1H NMR spectrum of a mixture of AgOTf, $Hg(OTf)_2$, and **2** in a 3:3:2 ratio displayed eight resonances (with equal values of the integrals) for the aromatic protons and two for the oxazolinyl protons, H^a (Figure 2e). These spectral patterns were totally different from that for either $[Ag_6\mathbf{2}_2]^{6+}$ or $[Hg_6\mathbf{2}_2]^{12+}$. The corresponding ESI-TOF mass spectrum showed only an intense signal at *m/z* 1351.5 assignable to $[Ag_3Hg_3\mathbf{2}_2\cdot(OTf)_6]^{3+}$ (Figure S5). These results clearly

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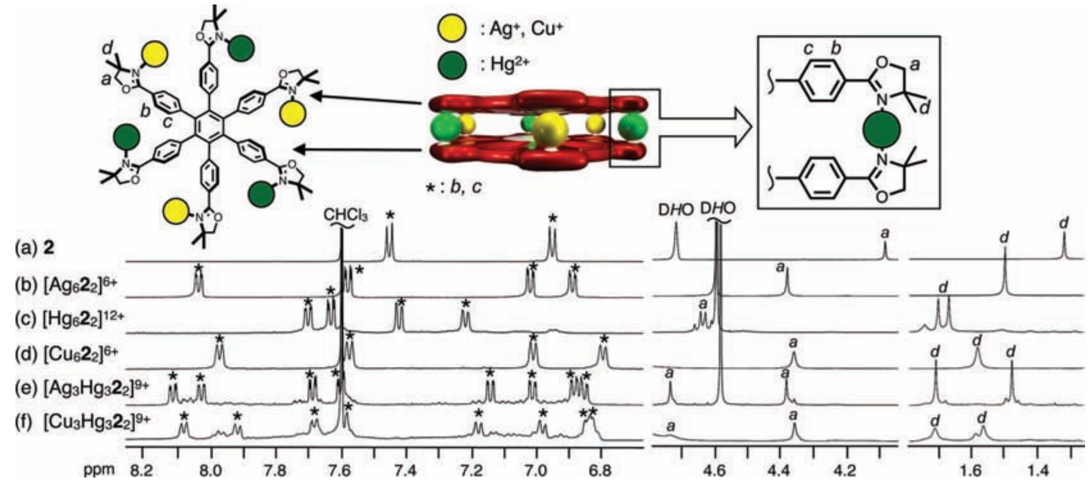

Figure 2. Partial ^{1}H NMR spectra (500 MHz, 303 K) of (a) **2**, (b) $[Ag_6\mathbf{2}_2]^{6+}$, (c) $[Hg_6\mathbf{2}_2]^{12+}$, (d) $[Cu_6\mathbf{2}_2]^{6+}$, (e) $[Ag_3Hg_3\mathbf{2}_2]^{9+}$, and (f) $[Cu_3Hg_3\mathbf{2}_2]^{9+}$ in 1:1 $CD_3OD/CDCl_3$ ([**2**] = 3.7 mM). Asterisks denote signals for the *p*-phenylene protons H^b and H^c.

indicate that two sets of oxazoline rings in different chemical environments are included in the resulting $[Ag_3Hg_3\mathbf{2}_2]^{9+}$ complex with C_3 symmetry. The only structure that meets this requirement is a sandwich-shaped $[Ag_3Hg_3\mathbf{2}_2]^{9+}$ complex in which three Ag^+ and three Hg^{2+} ions are alternately arranged.[6] The complexation of **2** with CuOTf and $Hg(OTf)_2$ gave comparable results. Eight aromatic and two oxazolinyl proton resonances appeared in the ^{1}H NMR spectrum (Figure 2f), and the ESI-TOF mass spectrum of the mixture displayed a signal at *m*/*z* 1307.2 assignable to $[Cu_3Hg_3\mathbf{2}_2\cdot(OTf)_6]^{3+}$ (Figure S6). In contrast, complexation of **2** with monovalent Ag^+ and Cu^+ ions resulted in a broadened ^{1}H NMR spectrum, and the ESI-TOF mass measurement of the solution exhibited mixed signals assigned to $[Ag_nCu_{6-n}\mathbf{2}_2\cdot(OTf)_4]^{2+}$ and $[Ag_nCu_{6-n}\mathbf{2}_2\cdot(OTf)_3]^{3+}$ ($n = 2-4$) (Figures S7 and S8). These results suggest that the electrostatic repulsions between the nearest-neighbor metal ions (Ag^+-Ag^+, Cu^+-Cu^+, and Ag^+-Cu^+) are not significant and therefore that Ag^+ and Cu^+ ions could be placed statistically on the six metal-binding sites on a circle between two ligands **2**.

The alternate arrangement is highly dependent on the solvent polarity.[7] For instance, the ^{1}H NMR spectrum of a 2:3:3 mixture of **2**, AgOTf, and $Hg(OTf)_2$ in CD_3OD only (Figure S4e) was significantly different from those of the aforementioned spectra of $[Ag_3Hg_3\mathbf{2}_2]^{9+}$, $[Ag_6\mathbf{2}_2]^{6+}$, and $[Hg_6\mathbf{2}_2]^{12+}$ in 1:1 $CD_3OD/CDCl_3$. The ESI-TOF mass spectrum of the mixture in CD_3OD showed only signals assigned to the $[Ag_3Hg_3\mathbf{2}_2]^{9+}$ complex, and no signals for $[Ag_nHg_{6-n}\mathbf{2}_2]^{(12-n)+}$ ($n = 0-6$) complexes were observed. These results suggest that the electrostatic repulsion between adjacent cationic metal ions should be reduced in a more polar solvent. As a result, the site selectivity becomes lower, and random arrangement of Ag^+ and Hg^{2+} ions takes place to form mixed $[Ag_3Hg_3\mathbf{2}_2]^{9+}$ complexes. With a decrease in the solvent polarity, the mixed resonances for the three possible $[Ag_3Hg_3\mathbf{2}_2]^{9+}$ isomers gradually changed into the eight aromatic resonances for a single $[Ag_3Hg_3\mathbf{2}_2]^{9+}$ complex in which the two types of ions are alternately arranged, as seen in 1:1 $CD_3OD/CDCl_3$. Furthermore, when the volume of $CDCl_3$ was more than half the total volume, new signals appeared, and eventually, all of the signals became broadened in $CDCl_3$ (Figure S4a,b). These results indicate that in extremely low polarity media, the electrostatic repulsion between adjacent Ag^+ and Hg^{2+} ions should become strong enough to destabilize the $[Ag_3Hg_3\mathbf{2}_2]^{9+}$ complex.

In summary, two kinds of metal ions with different charges but the same coordination geometry can be spontaneously arranged using a simple hexamonodentate ligand with six chemically and structurally equivalent coordination sites. The strategy described herein demonstrates that although all of the coordination sites are completely equivalent, the places of the metal ions can be precisely determined by virtue of the well-balanced relationship between the ligand affinities for each metal ion and electrostatic factors such as ion charges, counteranion identity, and solvent polarity.

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Supporting Information Available: Synthetic procedures, ^{1}H NMR spectra, and ESI-TOF mass spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(3) Metal complexation of **3** bearing six nonsubstituted oxazoline rings was not successful in solution under the same conditions because of the extremely low solubility of both the metal-free ligand and the resulting metal complexes.

(4) The $[Cu_6\mathbf{2}_2]^{6+}$ complex was stable under air for several months, while Cu(I) complexes generally are easily oxidized. Therefore, there was no need for special care in the preparation of this complex.

(5) The ^{1}H NMR spectrum of $[Hg_6\mathbf{2}_2]^{12+}$ differed from those for $[Ag_6\mathbf{2}_2]^{6+}$ and $[Cu_6\mathbf{2}_2]^{6+}$. For example, with $[Hg_6\mathbf{2}_2]^{12+}$, four resonances for the aromatic protons were found in the range of 7.2−7.5 ppm, and the two H^a and H^d protons in the oxazoline rings were inequivalent. This is probably due to structural differences, such as the helicity and/or conformational rigidity of the $[Hg_6\mathbf{2}_2]^{12+}$ complex.

(6) Diastereotopic proton signals for the oxazoline rings of $Ag_3Hg_3\mathbf{2}_2\cdot(OTf)_9$ complex were observed at 223 K, indicating that the complex has a helicity.

(7) The identity of the counteranion also affects the stability of the complexes. For example, when $N(CF_3SO_2)_2^-$ (NTf_2^-) was used as the counteranion, the stability of the $Ag_3Hg_3\mathbf{2}_2\cdot(NTf_2)_9$ complex, in which the two kinds of metal ions are alternately arranged, was lower than that of the triflate counterpart (Figure S10). Molecular modeling of the $[Ag_3Hg_3\mathbf{2}_2]^{9+}$ complex (Figure S11) suggests that the counteranions weakly interact with the linear two-coordinate Ag^+ and Hg^{2+} ions by the electrostatic force.

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