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Electrostatically Controlled Hierarchical Arrangement of Monocationic Silver(I) and Dicationic Mercury(II) Ions between Disk-Shaped Template Ligands

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Transition metal ions are ubiquitous constituents of functionalized materials with unique electronic, optical, magnetic, and catalytic properties. To date, many excellent studies have been reported on the metal array−function relationship, which have impressed us on the growing importance of developing novel chemical tools for metal arrays at the atomic level.[1] In particular, a precise control of heterogeneous metal array is a prerequisite for the construction of structurally and functionally more complex molecular architectures. In terms of the difficulty of synthesis, the heterogeneous metal array is much more difficult than the regular, homogeneous arrangement of metal ions; hence one has to devise ways to control the spatial configuration of metal centers, for instance, by making efficient use of programmable template ligands. Moreover, metal coordination geometries, hard/soft natures of metals and ligands, and electrostatic interactions between positively charged metal centers should be carefully considered in the design strategy.

We present herein a hierarchical arrangement of two kinds of metal ions that prefer a linear two-coordinate geometry on a two-dimensional (2D) plane using a disk-shaped hexa-monodentate ligand **1** in which three oxazoline rings are arranged on each of two concentric circles (Figure 1). ^{1}H NMR and electrospray ionization-time-of-flight (ESI-TOF) mass studies demonstrated the quantitative formation of a sandwich-shaped discrete structure, $Ag_3Hg_3\mathbf{1}_2$, in which three monocationic Ag^+ and three dicationic Hg^{2+} ions are site-selectively arranged on the two concentric circles from the center in this order.

Recently, we have reported the triangular array of three Ag^+ ions that prefer a linear two-coordinate geometry between two disk-shaped ligands **2** to form a sandwich-shaped $Ag_3\mathbf{2}_2$ complex quantitatively.[2] To extend this strategy to the hierarchical arrangement of two kinds of metal ions on a 2D plane between two disk-shaped ligands, we have designed a novel ligand **1** having six oxazoline rings, three of which (rings $\mathbf{G}^1$, the first generation coordination sites) are attached directly to the central benzene ring at the 1, 3, 5 positions, and the other three of which (rings $\mathbf{G}^2$, the second generation coordination sites) are arranged through a *p*-phenylene linker at the 2, 4, 6 positions in a concentric pattern. We expected that this ligand could arrange metal ions so as to minimize electrostatic repulsion between positively charged metal centers.

To learn first the metal binding nature of rings $\mathbf{G}^2$ in ligand **1**, the Ag^+ and Hg^{2+} complexation of a model ligand **3** having only three oxazolyl rings as $\mathbf{G}^2$ sites was examined. ^{1}H NMR titration with Ag^+ and Hg^{2+} and ESI-TOF mass measurements revealed that sandwich-shaped $Ag_3\mathbf{3}_2$ and $Hg_3\mathbf{3}_2$ complexes, respectively, are quantitatively formed in solution.[3] The ^{1}H NMR spectra for both complexes displayed eight resonances for eight aromatic protons of **3**, indicating the chemical environments of both sides of each oxazolyl ligand in the complexes are inequivalent, which strongly suggests the sandwich-shaped structure of $M_3\mathbf{3}_2$ complexes ($M =$ Ag^+ or Hg^{2+}) (Figure 2b and c, respectively). The resonances for the proton signals of oxazolyl rings, *a* and *b* of $Hg_3\mathbf{3}_2$, were located at 4.9 and 4.4 ppm, respectively, both of which shifted to downfield greater than those of $Ag_3\mathbf{3}_2$ as a result of the electron-deficient nature of Hg^{2+}. Thus, ^{1}H NMR is a good indicator for differentiating which binds to oxazolyl rings, Ag^+ or Hg^{2+}, in the isostructural sandwich-shaped complexes. On the other hand, ligand **4** having only three oxazolyl rings as $\mathbf{G}^1$ sites formed a sandwich-shaped structure only with Ag^+ to generate $Ag_3\mathbf{4}_2$ (Figure 2e),[4] whereas ligand **3** with only $\mathbf{G}^2$ sites formed both Ag^+- and Hg^{2+}-linked sandwich-shaped complexes. This specific formation of $Ag_3\mathbf{4}_2$ should arise from minimal electrostatic repulsion between monocationic Ag^+ arranged in a triangle within the complex. In addition, the ^{1}H NMR investigation of a mixed solution containing **3**, Ag^+, and Hg^{2+} in a 2:3:3 ratio revealed exclusive formation of $Hg_3\mathbf{3}_2$. These model studies clearly indicate that the binding specificity for Hg^{2+} and Ag^+ in the sandwich-shaped complexes M_3L_2 is completely different. Thus, the newly designed disk-shaped hexa-monodentate ligand **1** bearing six oxazoline rings as $\mathbf{G}^1$ and $\mathbf{G}^2$ sites was expected to establish hierarchical heterometal arrangement of Ag^+ and Hg^{2+} in a sandwich-shaped complex.

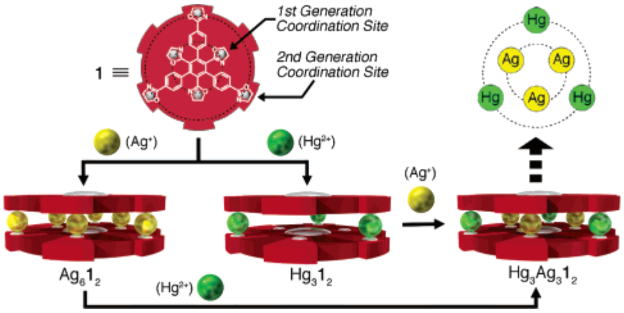

Figure 1. Schematic representation of hierarchical arrangement of Ag^+ and Hg^{2+} ions between two disk-shaped hexa-monodentate ligands **1**.

^{1}H NMR study clearly demonstrated the site-specific arrangement of monocationic Ag^+ and dicationic Hg^{2+} between two disk-shaped ligands **1**. Upon addition of 1.5 equiv of Hg^{2+} to a solution of **1** in a 1:1 mixed solvent of CD_3OD and $CDCl_3$, the proton signals of rings $\mathbf{G}^2$, *a* and *b*, were observed at 5.0 and 4.6 ppm, respectively, which are comparable to those of *g* and *h* of $\mathbf{G}^2$ sites in $Hg_3\mathbf{3}_2$. On the other hand, the proton signals of rings $\mathbf{G}^1$, *c* and *d*, showed almost no shifts, indicating that rings $\mathbf{G}^2$ bind exclusively to Hg^{2+} (Figure 2g).[5] ESI-TOF mass spectrum of the mixture displayed two signals at $m/z = 830.4$ and 1319.6, which are assignable to $[Hg_3\mathbf{1}_2\cdot(OTf)_3]^{3+}$ and $[Hg_3\mathbf{1}_2\cdot(OTf)_4]^{2+}$, respectively. We therefore conclude that three Hg^{2+} are put between two ligands **1** in a sandwich-shaped

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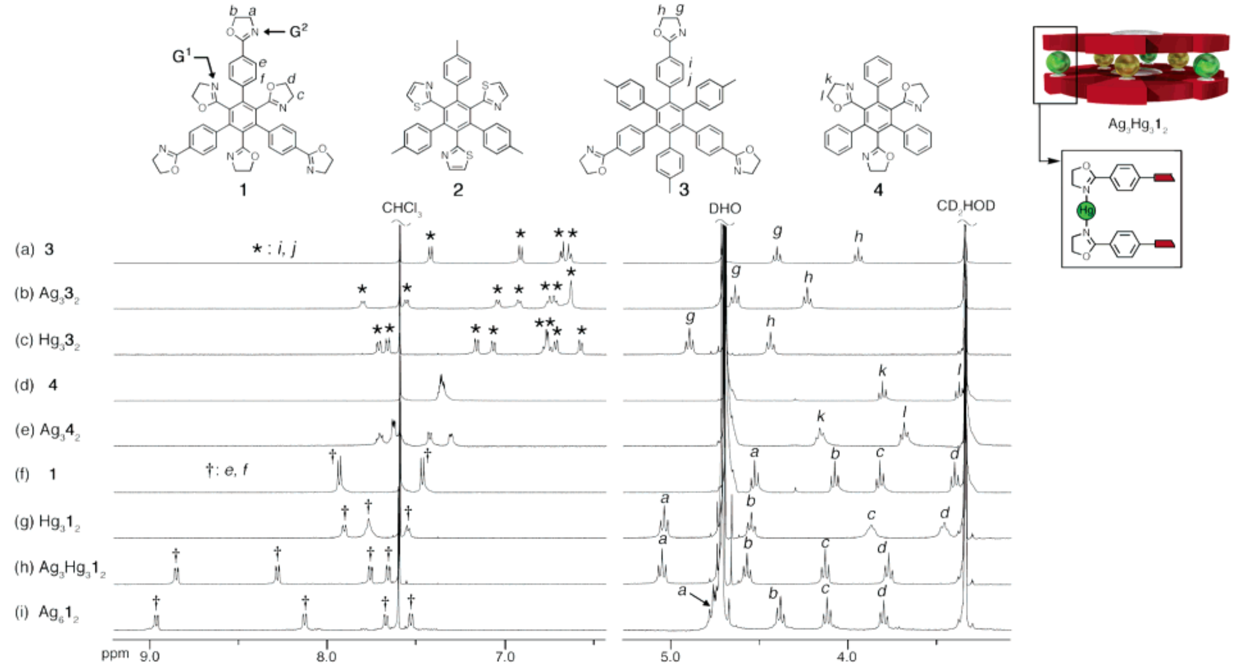

Figure 2. ^{1}H NMR spectra (500 MHz, $CD_3OD:CDCl_3 = 1:1$, 293 K, [**1**] = 2.0 mM, [**3**] = 4.1 mM, [**4**] = 3.2 mM).

$Hg_3\mathbf{1}_2$ complex and that three $\mathbf{G}^2$ oxazolyl rings coordinate to Hg^{2+}. Subsequent Ag^+ complexation with rings $\mathbf{G}^1$ was monitored by ^{1}H NMR spectroscopy. Upon addition of 3 equiv of Ag^+ to a solution of $Hg_3\mathbf{1}_2$, the ^{1}H NMR spectrum of the mixture displayed eight resonances, including four sets of phenylene protons and four sets of oxazolyl protons in a highly symmetrical manner (Figure 2h). It is notable that the protons of rings $\mathbf{G}^1$, *c* and *d*, shifted significantly to downfield, whereas those of rings $\mathbf{G}^2$ did not show any change after the first Hg^{2+} complexation, indicating that Ag^+ ions were selectively bound by rings $\mathbf{G}^1$ in the second complexation. ESI-TOF mass spectrum of the mixed solution also demonstrated the formation of a heterogeneous $Ag_3Hg_3\mathbf{1}_2$ complex, showing two signals at m/z = 1087.0 and 1704.9 assignable to $[Ag_3Hg_3\mathbf{1}_2\cdot(OTf)_6]^{3+}$ and $[Ag_3Hg_3\mathbf{1}_2\cdot(OTf)_7]^{2+}$, respectively. These results provide clear evidence that ligand **1** allows the quantitative, hierarchical assembly of Ag^+ and Hg^{2+} on the inner and outer circles of the two concentric circles, respectively.

To prove the advantage of this hierarchical array, a competition experiment was performed as follows. The complexation of **1** with 3 equiv of Ag^+ resulted in the quantitative formation of $Ag_6\mathbf{1}_2$ in which six Ag^+ ions are put between two ligands **1**, as characterized by ^{1}H NMR (Figure 2i) and ESI-TOF mass measurements.[6] It should be noted that three Ag^+ bound by rings $\mathbf{G}^2$ were selectively replaced by three Hg^{2+} to form $Ag_3Hg_3\mathbf{1}_2$ upon addition of 3 equiv of Hg^+ to $Ag_6\mathbf{1}_2$. The ^{1}H NMR spectrum of this mixed solution was identical to that of the aforementioned solution. This result can be best explained by the fact that relatively large electrostatic repulsion between dicationic Hg^{2+} allows the selective Ag^+ binding to $\mathbf{G}^1$ sites despite the thermodynamically preferable binding between the oxazolyl rings and Hg^{2+}.[7]

In summary, monocationic Ag^+ and dicationic Hg^{2+} were hierarchically assembled on a 2D plane formed between two disk-shaped hexa-monodentate ligands **1** to form a sandwich-shaped $Ag_3Hg_3\mathbf{1}_2$ complex. The two kinds of binding sites hierarchically arranged within **1** have a completely opposite affinity for these metal ions, though all of the ligands attached are structurally identical. This finding indicates that the metal affinity of each binding site in multi-monodentate ligands can be precisely controlled by the design strategies keeping electrostatic repulsion to a minimum.

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Supporting Information Available: Details of the ligand syntheses. ESI-TOF mass spectra of metal complexes. This material is available free of charge via Internet at http://pubs.acs.org.

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(3) ESI-TOF mass data for $Ag_3\mathbf{3}_2$: m/z 630.4 $[Ag_3\mathbf{3}_2]^{3+}$, 1020.0 $[Ag_3\mathbf{3}_2\cdot OTf]^{2+}$; for $Hg_3\mathbf{3}_2$: m/z 617.0 $[Hg_3\mathbf{3}_2\cdot(OTf)_2]^{4+}$, 872.0 $[Hg_3\mathbf{3}_2\cdot(OTf)_3]^{3+}$, 1383.5 $[Hg_3\mathbf{3}_2\cdot(OTf)_4]^{2+}$.

(4) No discrete structures were formed from **4** and Hg^{2+} as evidenced by ^{1}H NMR and ESI-TOF mass measurements. However, the ^{1}H NMR spectrum of a mixed solution of **4**, Hg^{2+}, and Ag^+ in a 2:3:3 ratio revealed the selective formation of the $Ag_3\mathbf{4}_2$ complex.

(5) Oxazolyl protons *a*−*d* of rings $\mathbf{G}^2$ and $\mathbf{G}^1$ of the ligand **1** were assigned according to data of model compounds **3** and **4** (Figure 2a and d).

(6) ESI-TOF mass datum for $Ag_6\mathbf{1}_2\cdot(OTf)_6$: m/z 845.0 $[Ag_6\mathbf{1}_2\cdot(OTf)_3]^{3+}$, 1341.9 $[Ag_6\mathbf{1}_2\cdot(OTf)_4]^{2+}$. See Supporting Information.

(7) The changes in polarity and ionic strength of the solvent did not affect the site selectivity of metal ions in $Ag_3Hg_3\mathbf{1}_2$ at all. Lattice energy calculations of six isomers of $Ag_3Hg_3\mathbf{1}_2$ indicate that the complex in which Ag^+ and Hg^{2+} ions are on the $\mathbf{G}^1$ and $\mathbf{G}^2$ sites, respectively, is most stable among other isomers. See Supporting Information.

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