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# Anion-Controlled Circular Dichroism Spectral Changes in $Hg^{2+}$ Complexes with a Chiral Bidentate Ligand

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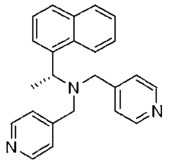
*Supporting Information*

**ABSTRACT:** Anion-controlled circular dichroism (CD) spectral changes in $Hg^{2+}$ complexes with a chiral bidentate ligand are reported. Although the $Hg(CF_3SO_3)_2$ and $Hg(CF_3CO_2)_2$ complexes with (*R*)-(−)-**1**-(naphthalen-1-yl)-*N*,*N*-bis(pyridin-4-ylmethyl)ethanamine, (*R*)-(−)-**1**, show significant CD spectral changes, no CD spectral changes were observed in the $HgCl_2$, $HgBr_2$, $Hg(CN)_2$, or $Hg(CH_3CO_2)_2$ complexes. X-ray analysis indicates that both the (*R*)-(−)-**1**-$Hg(CF_3SO_3)_2$ and (*R*)-(−)-**1**-$HgCl_2$ complexes form a coordination polymer and a discrete 2:3 [=(*R*)-(−)-**1**/$HgCl_2$] complex with a figure-eight structure. X-ray crystallography revealed that (i) the Hg−Hg distances bridged by anions vary depending on the anions used and (ii) a coordination polymer cannot be formed when the Hg−Hg distances are too short. Therefore, the formation of a coordination polymer is required to give the observed significant CD spectral changes.

It is well-known that anions play an important role in coordination chemistry.[1−13] In some cases, anions act as secondary ligands and affect the structures of the complexes. For example, Lee and Lee reported that the coordination ability of anions controls the whole structure of $Hg^{2+}$ complexes.[14] In their system, significant UV−vis spectral changes occur that depend on the anions in question.

Recently, we reported on a new $Hg^{2+}$-sensing system that is based on the structures of complexes.[15] The system uses the combination of a chiral bidentate ligand, (*R*)-(−)-**1**, and circular dichroism (CD) spectroscopy. Significant CD spectral changes were observed when $Hg^{2+}$ was added, whereas no CD spectral changes were observed in the cases of $Li^+$, $Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Mn^{2+}$, $Fe^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Rb^+$, $Ag^+$, $Cd^{2+}$, $La^{3+}$, $Gd^{3+}$, and $Pb^{2+}$. We report here that the system not only is useful for $Hg^{2+}$ ion sensing but also shows promise as an anion-sensing system in an organic solvent.



(*R*)-(−)-**1**

The complexing properties of (*R*)-(−)-**1** toward several $Hg^{2+}$ salts were examined based on metal-ion-induced CD and UV−vis spectral changes in methanol (Figure 1). In the CD spectra, free (*R*)-(−)-**1** exhibits a negative Cotton effect at $\lambda_{ext}$ = 225 nm. When equimolar amounts of $Hg(CF_3SO_3)_2$ and $Hg(CF_3CO_2)_2$ were added, significant spectral changes were observed at $\lambda_{ext}$ = 225 and 214 nm, whereas no CD spectral changes were observed upon the addition of equimolar amounts of $HgCl_2$, $HgBr_2$, $Hg(CN)_2$, and $Hg(CH_3CO_2)_2$. However, a slight change in the UV−vis spectra was observed upon the addition of $Hg(CF_3SO_3)_2$ and $Hg(CF_3CO_2)_2$, although no spectral changes were observed upon the addition of the other salts described. These results indicate that the CD spectral changes depend on the counteranions to the $Hg^{2+}$ ions.

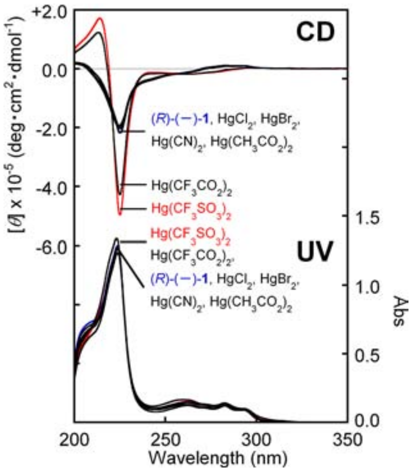


**Figure 1.** Hg salt-induced CD ([(*R*)-(−)-**1**] = $2.0 \times 10^{-4}$ M) and UV−vis ([(*R*)-(−)-**1**] = $1.9 \times 10^{-5}$ M in methanol) spectral changes.

In order to clarify the reasons behind this selectivity toward anions in the (*R*)-(−)-**1**/$HgX_2$ complexes, the structures of these complexes were examined by cold electrospray ionization mass spectrometry (ESI-MS) and $^1H$ NMR spectroscopy. The cold ESI-MS data for 1:1 mixtures of (*R*)-(−)-**1** and $HgX_2$ were measured in methanol. For example, the fragment ion peaks arising from $[(R)\text{-}(-)\text{-}\mathbf{1} + Hg^{2+} - H^+]^+$, $[2(R)\text{-}(-)\text{-}\mathbf{1} + 2Hg^{2+} + 2CF_3SO_3^-]^{2+}$, $[2(R)\text{-}(-)\text{-}\mathbf{1} + 2Hg^{2+} + 3CF_3SO_3^-]^+$, [4(R)-

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(−)-**1** + $4Hg^{2+}$ + $7CF_3SO_3^-]^+$, and [6(*R*)-(−)-**1** + $6Hg^{2+}$ + $10CF_3SO_3^-]^{2+}$ were observed at *m*/*z* 554, 703, 1555, 3259, and 2408, respectively, in a 1:1 mixture of (*R*)-(−)-**1** and $Hg(CF_3SO_3)_2$ (see Figure S1a,b in the Supporting Information, SI). The mass data indicate that the (*R*)-(−)-**1**/$Hg(CF_3SO_3)_2$ complex forms a 1:1$_n$ coordination polymer. On the other hand, the fragment ion peaks arising from [(*R*)-(−)-**1** + $Hg^{2+}$ + $Cl^-]^+$, [2(*R*)-(−)-**1** + $Hg^{2+}$ + $Cl^-]^+$, and [3(*R*)-(−)-**1** + $Hg^{2+}$ + $Cl^-]^+$ were observed at *m*/*z* 590, 943, and 1296, respectively, in a 1:1 mixture of (*R*)-(−)-**1** and $HgCl_2$ [Figure 2 (bottom)]. In addition, when 2 equiv of $HgCl_2$ was added, the fragment ion peak arising from [2(*R*)-(−)-**1** + $3Hg^{2+}$ + $3Cl^-$ − $2H^+]^+$ was also observed at *m*/*z* 1413 [Figure 2 (top)], although the intensity is very low. These results indicate that the (*R*)-(−)-**1**/$HgCl_2$ complexes form a discrete complex. The patterns for the fragment ion peaks of the (*R*)-(−)-**1**/$Hg(CF_3CO_2)_2$ and (*R*)-(−)-**1**/$HgX_2$ (X = $CH_3CO_2$, Br, CN) complexes are the same as those for the (*R*)-(−)-**1**/$Hg(CF_3SO_3)_2$ and (*R*)-(−)-**1**/$HgCl_2$ complexes (Figures S2a,b, S3a,b, S4a,b, S5a,b, and S6a,b in the SI).

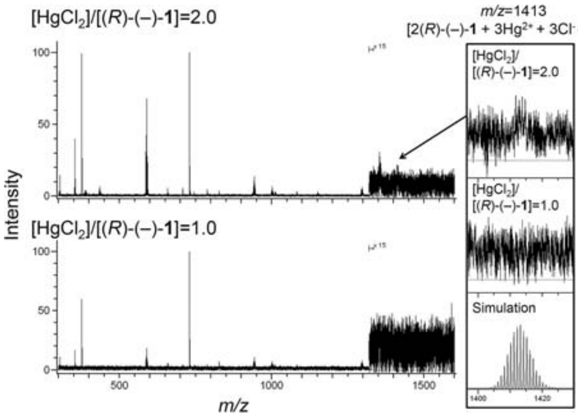

**Figure 2.** Cold ESI-MS of mixtures of (*R*)-(−)-**1** and $HgCl_2$ in methanol: (top) [$HgCl_2$]/[(*R*)-(−)-**1**] = 2.0; (bottom) [$HgCl_2$]/[(*R*)-(−)-**1**] = 1.0.

$^1H$ NMR titration experiments were carried out in methanol-$d_4$ (see Figures S7−S12 in the SI). When equimolar amounts of $Hg(CF_3SO_3)_2$ and $Hg(CF_3CO_2)_2$ were added, the signal widths of the pyridine protons broadened and the signals of the 8-position proton of the naphthalene and the methine proton of the chiral center shifted to lower field by about 0.6−0.7 ppm. These results suggest that the complexes are coordination polymers and that the naphthalene and methine protons are located in a deshielded area of the pyridine rings. On the other hand, when $HgX_2$ (X = $CH_3CO_2$, Cl, Br, CN) were added, slight (∼0.2 ppm) or no chemical shift changes in the naphthalene and methane protons were observed. Figure 3 shows the relationship between the $^1H$ NMR chemical shift changes of the 8-position proton of naphthalene and the intensity changes in the CD spectra. As shown in Figure 3, there is a correlation between the chemical shift changes in the $^1H$ NMR and the intensity changes in the corresponding CD spectra. This means that the anions control the whole structure of the $Hg^{2+}$ complexes with (*R*)-(−)-**1**.

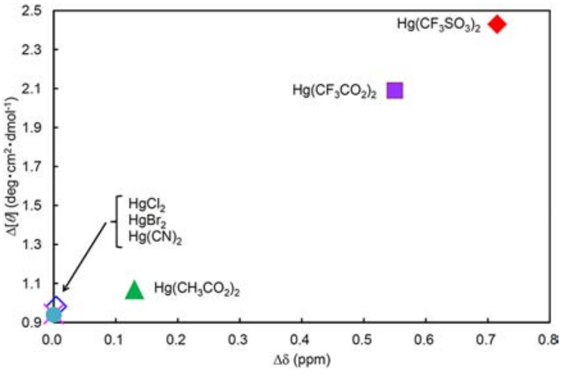

**Figure 3.** Correlation between $HgX_2$-induced CD intensity changes and chemical-shift changes: (red ◆) $Hg(CF_3SO_3)_2$; (purple ■) $Hg(CF_3CO_2)_2$; (green ▲) $Hg(CH_3CO_2)_2$; (blue ◇) $HgCl_2$; (pink ×) $HgBr_2$; (teal ●) $Hg(CN)_2$.

(*R*)-(−)-**1** in chloroform [for the $Hg(CF_3SO_3)_2$ complex] or dichloromethane (for the $HgCl_2$ complex) was treated with equimolar amounts of $Hg(CF_3SO_3)_2$ and $HgCl_2$ in methanol to give (*R*)-(−)-**1**/$Hg(CF_3SO_3)_2$ and (*R*)-(−)-**1**/$HgCl_2$ complexes, respectively, in quantitative yields. The structures of the $Hg(CF_3SO_3)_2$ and $HgCl_2$ complexes with (*R*)-(−)-**1** were determined by X-ray crystallography. As we reported in a previous paper[11] (also see Figure S13 and Table S1 in the SI), the (*R*)-(−)-**1**/$Hg(CF_3SO_3)_2$ complex is a zigzag polymer-like complex. The $Hg^{2+}$ ion is six-coordinated by the pyridine N2 and N3 atoms and the O1, O3, O4, and O5 atoms of the $CF_3SO_3$ anions. The N2(pyridine)−N1(amine)−N3(pyridine) angle and the Hg−Hg distance are ca. 52° and 5.3 Å, respectively. Interestingly, opposite $CF_3SO_3$ anions bridge two $Hg^{2+}$ ions to form a looped, one-dimensional network structure. The bidentate double-bridging anions play a crucial role as the backbone to the assembly of this unique and robust supramolecular network. The 8-position hydrogen in the naphthalene (colored pink in Figure S13d in the SI) and the methine hydrogen are located in the deshielded area of two pyridines. On the other hand, the (*R*)-(−)-**1**/$HgCl_2$ complex is a discrete 2:3 [=(*R*)-(−)-**1**/$HgCl_2$] complex with a figure-eight structure (Figure 4). Although some groups have reported 2:3 complexes (=ligand/$Hg^{2+}$),[16−18] this is the first example of a 2:3 complex by a bidentate ligand. There are two coordination modes in the $Hg^{2+}$ ions, where the middle $Hg^{2+}$ ion (Hg2) is six-coordinated by the pyridine N2 and N5 atoms, and the Cl2, Cl3, Cl4, and Cl5 atoms, and the end $Hg^{2+}$ ions (Hg1 and

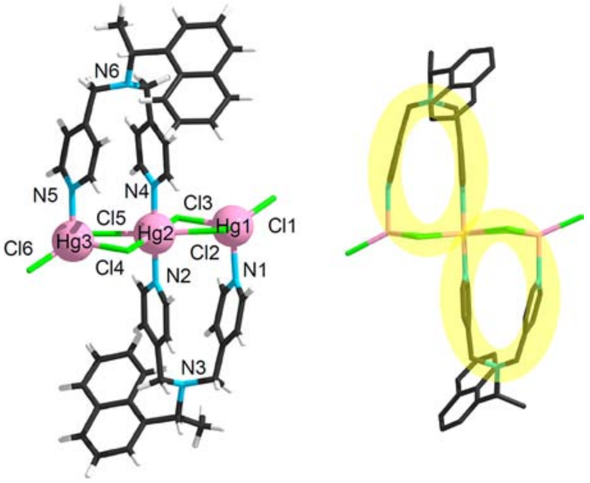

**Figure 4.** X-ray crystal structure of a discrete (*R*)-(−)-**1**/$HgCl_2$ complex with a figure-eight structure.

Hg3) are four-coordinated by the pyridine N1 (N4) atom, and the Cl1 (Cl6), Cl2 (Cl5), and Cl3 (Cl4) atoms. The Cl2, Cl3, Cl4, and Cl5 atoms bridge the end and middle $Hg^{2+}$ ions. In this complex, the N1(pyridine)−N3(amine)−N2(pyridine) angle and the Hg−Hg distance are ca. 44° and 3.9 Å, respectively, and the Hg−Hg distance in the (*R*)-(−)-**1**/$HgCl_2$ complex is much shorter than that in the (*R*)-(−)-**1**/$Hg(CF_3SO_3)_2$ complex (by ca. 1.4 Å). Because the Hg−Hg distance bridged by the $Cl^-$ ions is so short, the structure of the ligand should be unstable. The energies of the ligand components were calculated by ab initio and density functional theory methods, using the X-ray structures of the (*R*)-(−)-**1**/$Hg(CF_3SO_3)_2$ and (*R*)-(−)-**1**/$HgCl_2$ complexes as input (see Table S3 and Figure S15 in the SI).[19] The calculations suggest that the energy of each ligand component in the (*R*)-(−)-**1**/$HgCl_2$ complex is ca. 9 kcal/mol higher than that in the (*R*)-(−)-**1**/$Hg(CF_3SO_3)_2$ complex. Therefore, the (*R*)-(−)-**1**/$HgCl_2$ complex cannot form a coordination polymer such as that in the case of the (*R*)-(−)-**1**/$Hg(CF_3SO_3)_2$ complex, and exciton coupling[20,21] between the naphthalene units cannot occur. Hence, the (*R*)-(−)-**1**/$HgCl_2$ complex shows no CD spectral changes. The X-ray structure consequently supports the low intensity of the fragment ion peak arising from the 2:3 [=(*R*)-(−)-**1**/$HgCl_2$] complex at *m*/*z* 1413 by the cold ESI-MS.

These results indicate that the formation of a coordination polymer is required to give the observed significant CD spectral changes. It is well-known that the $CF_3SO_3^-$ ion is a weaker base than $Cl^-$, $Br^-$, $CN^-$, $CF_3CO_2^-$, and $CH_3CO_2^-$ ions. On the other hand, $CF_3SO_3^-$ and $CF_3CO_2^-$ ions have two or more O atoms in their molecules. Both the weak binding ability and the number of binding sites would be important to construct the coordination polymers.

In order to examine the effect of the anions on the structural changes, anion-exchange experiments using CD spectroscopy, $^1H$ and $^{19}F$ NMR, and cold ESI-MS were carried out (see Figures S16−S19 in the SI). When tetraethylammonium chloride was added to a 1:2 [=(*R*)-(−)-**1**/$Hg(CF_3SO_3)_2$] mixture in methanol (methanol-$d_4$ for $^1H$ and $^{19}F$ NMR), the spectral data arising from the (*R*)-(−)-**1**/$Hg(CF_3SO_3)_2$ complex changed to those of the (*R*)-(−)-**1**/$HgCl_2$ complex. Therefore, these data strongly support that the structures of the (*R*)-(−)-**1**/$HgX_2$ complexes are dependent on the counteranions involved.

In summary, we have demonstrated that the new (*R*)-(−)-**1** ligand is useful as an anion-sensing system in an organic solvent. The significant changes in the CD spectra were shown to be dependent on the anions in the system. The combination of a chiral ligand and CD spectroscopy provides a route to new cation- and anion-sensing systems.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Crystallographic data in CIF format of (*R*)-(−)-**1**-$HgCl_2$ complex, experimental procedures, spectral data, and titration and anion-exchange experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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