Effect of Countercations on the Structural Isomerization of a Dianionic Diruthenium Complex with a Ligand-unsupported Ru–Ru Bond

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Isomers of $[Ru_2^{III,III}(3,5\text{-DTBCat})_4]^{2-}$ ($3,5\text{-DTBCat}^{2-}$ = 3,5-di-*tert*-butylcatecholate) were successfully characterized. It is found that the isomerization from the kinetically stable cis,cis form to the thermodynamically stable trans,trans form is caused not only by heating but also by the cation exchange from Na^+ to $n\text{-}Bu_4N^+$, revealing that the isomerization is regulated by the specific cation–anion interactions.

Considerable attention has been paid for metal–metal bonded diruthenium complexes because they afford not only a variety of electronic properties[1] but also unique structures including isomers.[1a,2] On the investigations of the effect of isomeric forms, paddle-wheel type complexes are particularly focused. However, the structural rigidity ascribed to bridging ligands, restricts the isomerization around a Ru–Ru bond, reducing the degree of freedom. It is useful to take advantages of ligand-unsupported Ru–Ru bonded complexes for their less structural restriction on isomerization and higher potential to form several isomers. Thus, studies on such complexes would provide a great opportunity to develop the molecular functional materials based on the structural and electronic flexibility.

Recently, a novel type of diruthenium complex with a ligand-unsupported Ru–Ru bond, $[Na_2\{Ru_2^{III,III}(3,5\text{-DTBCat})_4\}]$ ($3,5\text{-DTBCat}^{2-}$ = 3,5-di-*tert*-butylcatecholate), has been synthesized and structurally characterized.[3a] This complex containing asymmetrical chelate ligands possesses two $[Ru(3,5\text{-DTBCat})_2]$ units connected by a Ru–Ru bond, and could, in principle, afford several isomers depending on the cis–trans configuration of each $[Ru(3,5\text{-DTBCat})_2]$ unit. In fact, *cis,cis*-$[\{Na(DME)_2\}_2\{Ru_2(3,5\text{-DTBCat})_4\}]$ (**1**•4DME; DME = 1,2-dimethoxyethane), whose two 3,5-DTBCat chelate to each Ru atom in a cis form, was selectively synthesized by the reaction in THF (THF = tetrahydrofuran) at rt and isolated as single crystals.[3a] Furthermore, the selective formation of a cis,cis isomer is independent on the size of the alkali-metal ions (Li^+, Na^+, K^+, and Rb^+) contained as countercations.[3b] However, the trans,trans isomer would be thermodynamically stable since mononuclear analogues free of interligand interactions are known to be stabilized in a trans form.[4] This indicates that the cation binding property is another important factor to control the isomeric forms of the complexes that two asymmetric bidentate ligands coordinate to a metal ion in square-planar arrangement, although the isomeric forms have been controlled by interligand π–π interactions[5] or hydrogen-bonding interactions.[6] Here, we focus on the role of countercations to regulate the isomerization based on the cis–trans configuration of asymmetric chelate ligands.

To improve the isolation yield of the cis,cis isomer in the synthesis of **1**•4DME at rt,[3a] the solution behavior of this sample was investigated at rt. For the ^1H NMR spectrum of **1** in THF-d_8, two peaks at 6.52 and 6.31 ppm are assigned to the aromatic protons of 3,5-DTBCat (Figure 1a). Heating a THF solution of **1** up to 50 °C, the isomerization of **1** proceeded, and a mixture of **1** and other compounds was obtained (See Supporting Information). This isomerization was completed in a day, and following evaporation to dryness afforded a violet sample (**2**) whose ^1H NMR spectrum is obviously different from that of **1** (Figure 1b). Complexes **1** and **2** maintained their original ^1H NMR spectra for a week at rt. This indicates both of **1** and **2** rarely isomerize in THF at rt.

The recrystallization of **2** from Hex/THF (Hex = *n*-hexane)

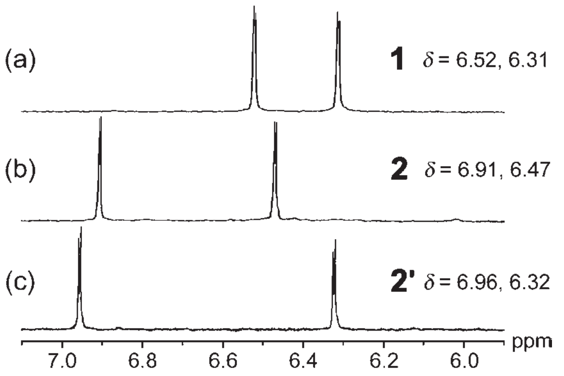

Figure 1. ^1H NMR spectra of (a) **1**, (b) **2**, and (c) **2′** in THF-d_8 at rt.

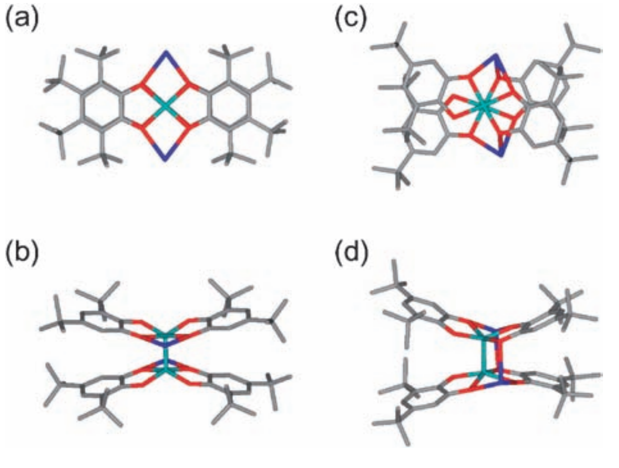

Figure 2. Structures of dinuclear complexes in (a, b) **1**•4THF•$2H_2O$ and (c, d) **2**•4THF•$2H_2O$. Hydrogen atoms and cocrystallized solvent molecules are omitted for clarity. Color code; Ru: green, Na: blue; C: gray, O: red.

at rt afforded single crystals of a *trans*,*trans*-$[\{Na(THF)_2\}_2\{Ru_2(3,5\text{-}DTBCat)_4\}]$ (**2**•4THF),[7] while the recrystallization of a sample obtained by the reaction between $Ru_2(OAc)_4Cl$ and 3,5-DTBCatH_2 under the same condition afforded a *cis*,*cis*-$[\{Na(THF)_2(H_2O)\}_2\{Ru_2(3,5\text{-}DTBCat)_4\}]$ (**1**•4THF•$2H_2O$).[7] This indicates that the cis,cis isomer (**1**) turned to the trans,trans isomer (**2**) by heating. The structures of these compounds are depicted in Figure 2. Both Ru atoms in these compounds commonly have no ligands or solvents on the apical positions, demonstrating distorted square-pyramidal coordination geometry. The dinuclear complexes in **1**•4THF•$2H_2O$ and **1**•4DME[3a] are isostructural while the structure of dinuclear complex in **2**•4THF with a twist angle of 40.9° is evidently different from those of **1**•4DME and **1**•4THF•$2H_2O$. The Ru–Ru bond distance of **2**•4THF, 2.1488(9) Å, is shorter than those of **1**•4DME (2.1698(6) Å)[3a] and **1**•4THF•$2H_2O$ (2.1747(4) Å), and comparable to that of $[\{Na(THF)_2\}_2Ru_2(3,6\text{-}DTBCat)_4]$ (2.140(1) Å) with a twist angle of 50°.[3a] This indicates that the twist along the Ru–Ru axis could decrease the repulsion between the O atoms of 3,5-DTBCat, as previously reported for the rotational isomers of $[(OEP)MoRu(TPP)]^+$ (OEP = octaethylporphyrin, TPP = tetraphenylporphyrin).[8] This twist changes the geometrical relationship between the opposite 3,5-DTBCat rings in a dimer and, therefore, the chemical shifts affected by the magnetic anisotropic effects of aromatic ligands[9] show considerable difference upon isomerization from **1** to **2** (Figure 1).

As shown in Figure 2, the Na^+ cations in both complexes bind to the O_{Cat} atoms. In order to reveal the role of the Na^+ cations on the selective formation of **1** and the isomerization from **1** to **2**, **1**•4DME was reacted with n-Bu_4NBr in THF at rt. Successful cation exchange from Na^+ to n-Bu_4N^+ afforded $(n\text{-}Bu_4N)_2[Ru_2(3,5\text{-}DTBCat)_4]$ (**2′**)[10] whose ^1H NMR spectrum in THF-d_8 at rt shows two peaks derived from the aromatic protons of 3,5-DTBCat at $\delta = 6.96$ and 6.32 ppm (Figure 1c). The chemical shifts of **2′** are obviously different from those of **1** and **2**. On the other hand, the spectra of **2** and **2′** measured in DMF-d_7 (DMF = *N*,*N*-dimethylformamide) are quite similar to one another although the countercations of **2** and **2′** are different and the cation exchange from **1** to **2′** was achieved without heating (Figures 3b and 3c). This could be due to the fact that the electrostatic interactions between the countercations and $[Ru_2(3,5\text{-}DTBCat)_4]^{2-}$ are extremely weakened in highly polar solvent,[3b] affording isostructural *trans*,*trans*-$[Ru_2(3,5\text{-}DTBCat)_4]^{2-}$. The most important point is that the cation exchange at rt accompanies the isomerization of $[Ru_2(3,5\text{-}DTBCat)_4]^{2-}$ from the cis,cis to the trans,trans form. Additionally, the spectrum of **2′** shows that the steric hindrance between two $[Ru(3,5\text{-}DTBCat)_2]$ units prevents the cis–trans equilibrium reaction found on the mononuclear analogue with no intramolecular interligand interaction.[11]

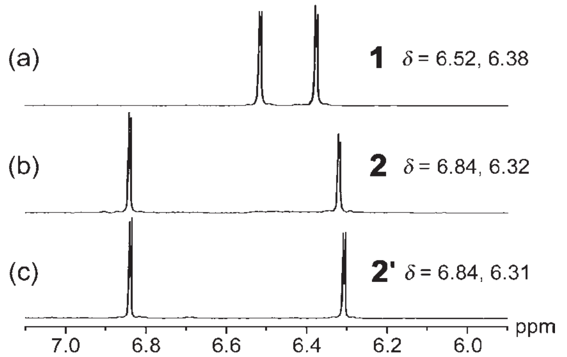

Figure 3. ^1H NMR spectra of (a) **1**, (b) **2**, and (c) **2′** in DMF-d_7 at rt.

In conclusion, the structural isomerization of the Ru–Ru bonded complex was performed not only by heating but also by the cation exchange from Na^+ to n-Bu_4N^+. This means that the cation–anion interaction effects on the isomerization from the kinetically stable cis,cis form to the thermodynamically stable trans,trans form. Therefore, the cation–anion interaction is regarded as an important factor to control the isomeric forms.

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7 Crystal Data for **1**•4THF•$2H_2O$: $C_{72}H_{116}Na_2O_{14}Ru_2$, fw = 1453.82, monoclinic, space group $C2/c$ (# 15), $a = 30.707(4)$, $b = 21.629(4)$, $c = 11.928(1)$ Å, $\beta = 97.048(7)°$, $V = 7862(1)$ Å^3, $T = 223$ K, $Z = 4$, $D_{calcd} = 1.228$ g cm^{-3}, 6585 unique ($I > 3.0\sigma(I)$), $R = 0.044$, $wR = 0.067$ (F, $I > 3.0\sigma(I)$). Crystal Data for **2**•4THF: $C_{72}H_{112}Na_2O_{12}Ru_2$, fw 1417.79, orthorhombic, space group $P2_12_12_1$ (# 19), $a = 14.013(2)$, $b = 19.688(3)$, $c = 27.351(5)$ Å, $V = 7545(2)$ Å^3, $T = 223$ K, $Z = 4$, $D_{calcd} = 1.248$ g cm^{-3}, 7261 unique ($I > 3.0\sigma(I)$), $R = 0.064$, $wR = 0.086$ (F, $I > 3.0\sigma(I)$). Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-000000 and CCDC-000000. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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10 The recrystallization of **2′** from Hex/THF afforded a single crystal. The structures of $[Ru_2(3,5\text{-}DTBCat)_4]^{2-}$ in **2**•4THF and **2′** are isostructural (See Supporting Information).

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