Different Magnetic Properties for Diastereomers of Alkoxide-bridged (*β*-Diketonato)ruthenium(III) Binuclear Complexes

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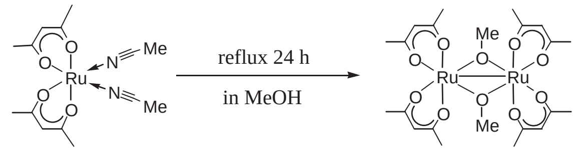
Symmetric alkoxide-bridged diruthenium complexes $[\{Ru(acac)_2\}_2(\mu\text{-}OMe)_2]$, which are obtained when $[Ru(acac)_2(CH_3CN)_2]$ reacts in methanol, can be separated into two diastereomers by column chromatography, and these diastereomers are found to exhibit different magnetic properties despite their structural similarities.

A tris(bidentate) metal complex $[M(bidentate)_3]^{n+}$ has two optical isomers with Δ and Λ conformations. Thus, a dimer of a tris(bidentate) metal complex has two stereoisomers with a racemic mixture (rac; $\Delta\Delta$, $\Lambda\Lambda$) and a meso form (meso; $\Delta\Lambda$) by combining Δ and Λ configuration moieties. A few reports have investigated the separation of this diastereomer because of its poor steric differences and, hence, difficulty in separation. Although Keene and co-workers separated and characterized polypyridyl diruthenium complexes bridged by 2,2′-bipyrimidine derivatives, no apparent differences were found in the properties between the diastereomers.[1] In contrast, spectral and/or electrochemical differences have been reported among diastereomers in which complexes were bridged by flexible multidentate ligands or two monodentate ligands.[2] Several binuclear (*β*-diketonato)diruthenium complexes have been prepared and characterized,[3] and there have been a few reports on the separation of their diastereomers.[4]

In this paper, we report the unexpected magnetic properties of alkoxide-bridged (acetylacetonato)diruthenium complexes $[\{Ru(acac)_2\}_2(\mu\text{-}OMe)_2]$ (**1**), which were successfully separated into two diastereomers by silica-gel-column chromatography. These diastereomers exhibited different magnetic properties. To the best of our knowledge, this is the first example where symmetrical (*β*-diketonato)diruthenium complexes show a marked difference in their magnetic properties in relation to the geometrical difference of diastereomers. Lahiri and co-workers reported for a similar complex $[\{Ru(acac)_2\}_2(\mu\text{-}OEt)_2]$.[5] However, they reported only the meso isomer, and its racemic isomer was not taken into consideration.

The reaction of $[Ru^{II}(acac)_2(CH_3CN)_2]$[6] in methanol produces methoxide double-bridged diruthenium complexes **1** (Scheme 1).[13] Diastereomers were separated by column chromatography, and the rac or meso structures were determined by using X-ray single-crystal analysis. No isomerisation was noted for **1r** and **1m** by refluxing in methanol for 24 h. The racemic mixture **1r** obtained was optically resolved by being eluted on a HPLC column packed with an ion-exchanged adduct of Δ-$[Ru(phen)_3]^{2+}$ and synthetic hectorite (Ceramosphere RU-1, Shiseido Co., Ltd., Japan).[7] The CD spectra obtained from the $\Lambda\Lambda$-enantiomers and $\Delta\Delta$-enantiomers (Figure S1[13]) indicate symmetrical shapes. Stereoisomers were assigned by referring to literature values.[8]



$[Ru(acac)_2(CH_3CN)_2]$ $[\{Ru(acac)_2\}_2(\mu\text{-}OMe)_2]$ (**1**)

Scheme 1. Synthesis of **1**.

Structures of **1** were confirmed by X-ray single-crystal analysis.[9,13] Figure 1 shows ORTEP diagrams. The Ru–Ru bonds has a distance of about 2.65 Å, and this length is similar to those observed in tetrachlorocatecholate diruthenium complexes bridged with alkoxide.[10] Although the structural parameters of diastereomers are mostly similar, the geometries of the relative orientation of the terminal acac rings between the **1r** and meso form **1m** are apparently different; by taking account of the direction of the methyl group in methoxide, **1r** should be pseudo C_2 structure in which the pseudo C_2 axis is perpendicular to Ru–Ru axis, while **1m** is the C_{2h} symmetry pocessing the center of inversion on the center of Ru–Ru bond. Such geometrical differences in the diastereomers also existed in the bridging $\{Ru_2O_2\}$ moiety; the four-membered ring of the **1r** is bent at the Ru–Ru bond, while the same ring of the **1m** is almost planar.

The ^1H NMR spectra of dinuclear complexes and their chemical shifts are shown in Figures S2 and S3.[13] Ruthenium(III) complexes generally exhibit a paramagnetic property because of a d^5 low-spin configuration in the metal center. Thus, the paramagnetic shift based on an unpaired electron of the

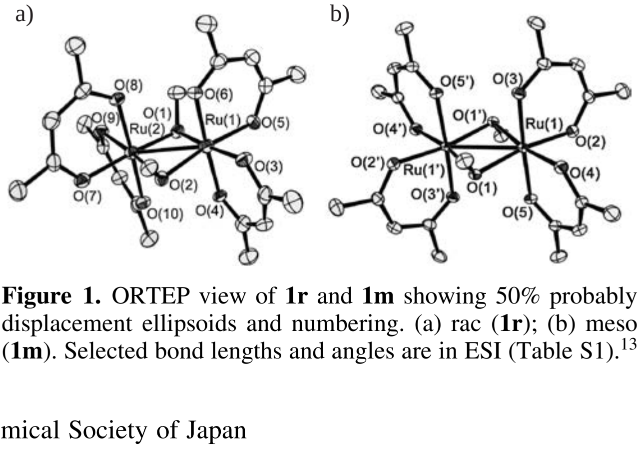


Figure 1. ORTEP view of **1r** and **1m** showing 50% probably displacement ellipsoids and numbering. (a) rac (**1r**); (b) meso (**1m**). Selected bond lengths and angles are in ESI (Table S1).[13]

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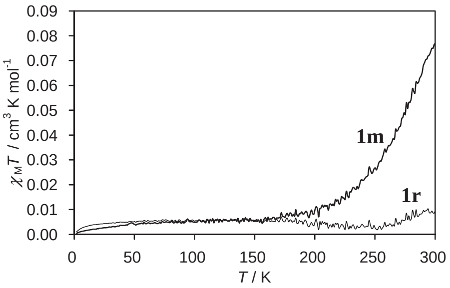

Figure 2. Magnetic property of **1**.

ruthenium(III) can be seen in the ^{1}H NMR spectra.[11] However, the alkoxide-bridged complexes [{Ru(acac)$_2$}$_2$(μ-OMe)$_2$] exhibited a diamagnetic shift in the racemic isomer and a slight paramagnetic shift in the meso isomer; the chemical shifts ranged from 0 to 8 ppm for the **1r** and from −5 to 30 ppm for the **1m**. This indicates that two unpaired electrons in both ruthenium(III) centers were coupled. For the diastereomers of ruthenium(III) dinuclear complexes, the ^{1}H NMR spectra are generally different owing to differences in their geometries, but this difference is known to be very small. However, in case of **1**, an abnormally large difference was found in the ^{1}H NMR spectra of the diastereomers. This is a unique magnetic property of complex **1**.

The $\chi_M T$ vs. T plots of the **1r** and **1m** are shown in Figure 2.[12] At 150 K, the **1r** and **1m** exhibited almost diamagnetic properties. However over 150 K, the $\chi_M T$ of the **1m** started increasing largely, while the **1r** still exhibited diamagnetic properties. At the room temperature, the $\chi_M T$ of the **1m** was estimated to be 0.1 cm^3 K mol^{-1}, which is in accordance with the chemical shift seen in the ^{1}H NMR spectra. These magnetic susceptibilities were not so large compared with that of a Ru^{III} d^5 low-spin paramagnetic complex (e.g., $\chi_{M([Ru(acac)3])}T =$ 0.45 cm^3 K^{-1} mol^{-1} at 300 K). Thus, two t$_{2g}$ orbitals of Ru^{III} were considered to have an antiferric overlap ($\sigma^2\pi^2\delta^2\delta^{*2}\pi^{*2}$). However, the coupling strength of the two Ru^{III} orbitals for the **1r** and **1m** may be slightly different owing to their geometric differences: The energy gap between HOMO and LUMO ($= \pi^*/\delta^*$ and σ^*) for **1m** is smaller than that for **1r**, so that **1m** can take triplet state easier than **1r** (Figure S5[13]). This antiferric coupling has not been observed in Ru^{II} dimer complexes, such as Ru–bpy system.[1]

In conclusion, we heve found that the alkoxide-bridged (acetylacetonato)diruthenium complexes [{Ru(acac)$_2$}$_2$(μ-OMe)$_2$] exhibited significantly different magnetic properties in relation to the geometrical difference of diastereomers. Further progress in designing the additional alkoxide dimers and their characterization are actively underway in our laboratory.

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