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Reaction of Tris(β-diketonato)ruthenium(III) Complexes with Strong Acids in Acetonitrile. Formation of Bis(acetonitrile)bis(β-diketonato)ruthenium(III) Complexes

Yuko KASAHARA, Yoshimasa HOSHINO,† Kunio SHIMIZU,* and Gen P. SATÔ
Department of Chemistry, Faculty of Science and Technology, Sophia University, Kioicho 7-1, Chiyoda-ku, Tokyo 102

Bis(acetonitrile)bis(β-diketonato)ruthenium(III) was readily formed through the reaction of the corresponding tris(β-diketonato) ruthenium(III) with perchloric, sulfuric, or hydrochloric acid in acetonitrile. The reaction was quantitative; the stoichiometry was 1:1 for each strong acid studied here. This reaction was employed to prepare several bis(acetonitrile)bis(β-diketonato)ruthenium(III) complexes, which proved to be convenient intermediates for the synthesis of mixed-ligand β-diketonato ruthenium(III) complexes of the $[Ru^{III}L_2L']$ type.

Kobayashi et al.[1] have reported that bis(acetonitrile)bis(β-diketonato)ruthenium(II) complexes could be prepared by reducing the corresponding tris(β-diketonato)ruthenium(III) with zinc amalgam in an acetonitrile–ethanol–water mixture and that these bis(acetonitrile) complexes were useful intermediates for the synthesis of mixed-ligand β-diketonato ruthenium(III) complexes of the $[Ru^{III}L_2L']$ type.

Here we describe a new and simple method for the preparation of bis(acetonitrile)bis(β-diketonato)ruthenium(III) through a ligand replacement reaction of tris(β-diketonato)ruthenium(III), which is induced by a strong acid:

$$[Ru^{III}L_3] + 2CH_3CN + H^+ \longrightarrow [Ru^{III}L_2(CH_3CN)_2]^+ + HL.$$
(L = β-diketonate ion)

When a small amount of concentrated perchloric acid was added to an acetonitrile solution of $[Ru^{III}(dpm)_3]$ (dpm^- = 2,2,6,6-tetramethyl-3,5-heptanedionate ion), the color of the mixture at once turned from orange to bluish purple. The isolation and identification of the product, $[Ru^{III}(dpm)_2(CH_3CN)_2]ClO_4$ (a new compound) are described below. The stoichiometry of the reaction was determined by means of spectrophotometric titration. An acetonitrile solution containing 5.0 μmol of $[Ru^{III}(dpm)_3]$ was titrated with perchloric acid (acetonitrile solution),

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†Present address: Nihon University, College of Pharmacy, 7-7-1, Narashinodai, Funabashi 274.

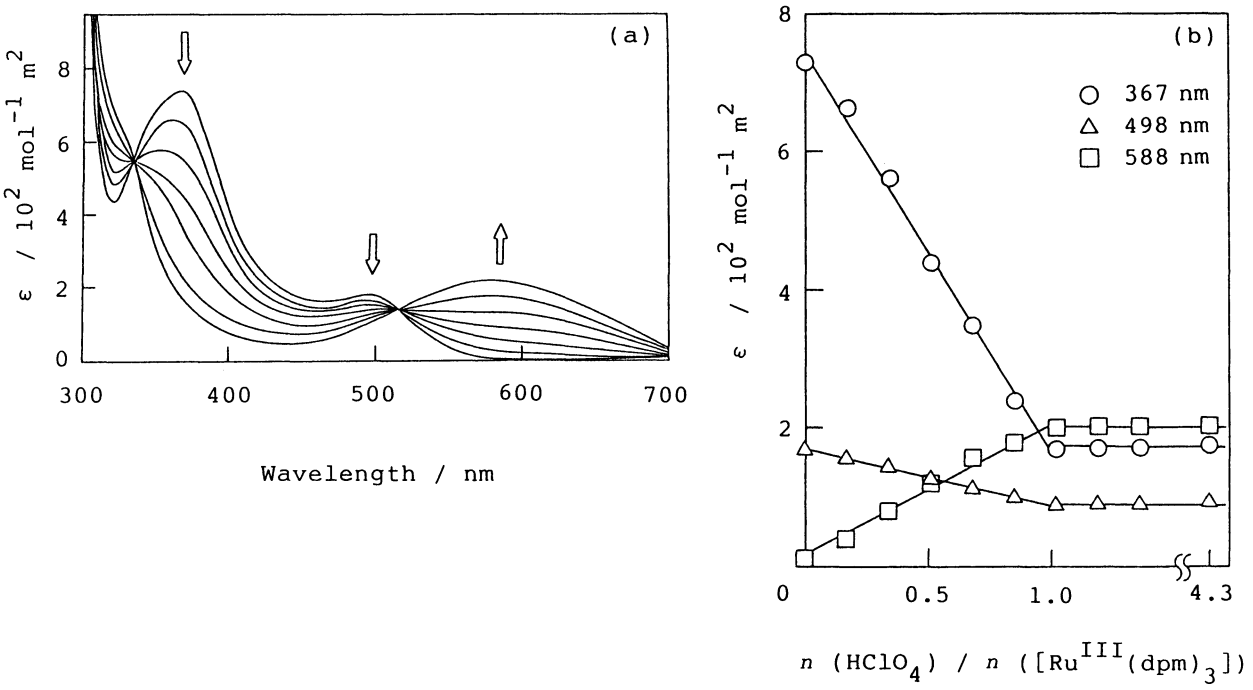

Fig. 1. Photometric titration of $[Ru^{III}(dpm)_3]$ with perchloric acid. (a) Spectral change. 0.5 mol m^{-3} $[Ru^{III}(dpm)_3]$ in acetonitrile, optical path 1 mm. (b) Titration curve. *n* is the amount of the substance specified. *n* ($[Ru^{III}(dpm)_3]$) = 5 μmol.

(Fig. 1a). The titration curves (Fig. 1b) show that the stoichiometry was 1:1. The reaction was quantitative and no further replacement occurred.

The reaction with sulfuric acid (it acted as a monoprotic acid) or hydrochloric acid was qualitatively the same: $[Ru^{III}(dpm)_2(CH_3CN)_2]^+$ was produced in either case. But the rates of these reactions were much slower than in the case of perchloric acid, and a large excess of the acid was required to complete either of the reactions in a reasonable time. This difference can be explained by the fact that the acid dissociation constant of perchloric acid in acetonitrile is larger than that of the other two acids.[2)]

A similar reaction took place in benzonitrile: the color of a benzonitrile solution of $[Ru^{III}(dpm)_3]$ turned bluish purple on the addition of perchloric acid. The product is probably a bis(benzonitrile) complex, but its identification is not yet definite. No reaction was observed in ethanol, dimethylsulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), pyridine, or benzene.

A new bis(acetonitrile) complex was isolated as follows. To 300 cm^3 of an acetonitrile solution containing 0.72 g of $[Ru^{III}(dpm)_3]$, a 20% excess of perchloric acid (70% aqueous solution) was added. After the mixture was stirred at room temperature for 1 h, the solvent was removed by evaporation. The residue was collected on a glass filter and was washed with water and hexane successively in order to remove excess perchloric acid and the dissociated ligand. The resulting

bluish purple crystals were dried under a vacuum (yield, 0.62 g or 87%). The compound was identified as $[Ru^{III}(dpm)_2(CH_3CN)_2]ClO_4$ by means of the elemental analyses, the IR spectrum, and the ^1H NMR spectrum.[3)]

This procedure was applicable to the preparation of other tris(β-diketonato)-ruthenium(III) complexes. For example, a new compound $[Ru^{III}(acac)_2(CH_3CN)_2]ClO_4$ ($acac^-$ = acetylacetonate ion), was synthesized in a similar manner. But the reaction was slower, and the mixture had to be refluxed for ca. 1 h. The residue obtained after the removal of acetonitrile was washed with hexane and then dissolved in water (the product was fairly soluble in water). The complex was extracted from the aqueous solution with dichrolomethane. Bluish purple crystals[4)] were obtained by evaporating the solvent (yield, 81%).

Bis(acetonitrile)bis(β-diketonato)ruthenium(III) complexes are useful intermediates for the synthesis of mixed-ligand β-diketonato ruthenium(III) complexes because the acetonitrile ligands can be replaced by other β-diketonate ions as easily as those of the corresponding ruthenium(II) species.[1)] For example, a new compound $[Ru^{III}(acac)(dpm)_2]$ was synthesized from $[Ru^{III}(dpm)_2(CH_3CN)_2]ClO_4$. The bis(acetonitrile) complex (0.50 g) was dissolved in a mixture of 90 cm^3 of ethanol and 10 cm^3 of water. After the addition of 0.08 g of Hacac and 0.08 g of $KHCO_3$, the solution was refluxed for 15 min and then evaporated to dryness. The solid was dissolved in benzene and subjected to column chromatography (Merck Kieselgel 60; benzene). The fraction of the first, orange band was collected. Orange crystals[5)] were obtained when benzene was evaporated off (yield, 0.34 g or 80% on the basis of the bis(acetonitrile) complex). Another example is $[Ru^{III}(acac)_2(dpm)]$.[1, 6)] This complex was prepared by treating $[Ru^{III}(acac)_2(CH_3CN)_2]ClO_4$ with Hdpm and $KHCO_3$ in the same way as described above (yield, 71%).

The above method appears to be preferable to that through bis(acetonitrile)-bis(β-diketonato)ruthenium(II) intermediates.[1)] The operations are much simpler and the yields are higher. Moreover, this method can dispense with zinc amalgam, which may be an environmental hazard.

The mechanism of the reaction of tris(β-diketonato)ruthenium(III) with a strong acid is not yet clear. It is certain, however, that this reaction is initiated by the attack at an Ru-O bond by protons, because the reaction would be extremely slow at room temperature if the breakage of Ru-O bond were the first step of the reaction: only trifluoromethyl-substituted tris(β-diketonato)ruthenium(III) complexes can undergo the *facial - meridional* isomerization, which is believed to take place through the rupture of an Ru-O bond, and the rates of their isomerization reactions are of the order of 10^{-4} s^{-1} at 100 °C in DMF.[7)]

A pathway similar to that proposed for the ligand exchange of $[Co^{III}(acac)_3]$, will probably be operative (Fig. 2).[8)] An intermediate with a dangling ligand (**2**) is formed by the proton attack. If the solvent is a strongly coordinating agent, the vacant site will be occupied by a solvent molecule, and the dangling ligand will finally dissociate, allowing an acetonitrile molecule to coordinate at the adjacent position. But we cannot explain why no reaction took place in DMSO or in DMF, which can coordinate to ruthenium(III).[9-12)] The fact that only one β-diketonato ligand was replaced even in the presence of more than 100 fold excess of

acid is also difficult to account for, although this is advantageous from the viewpoint of synthesis.

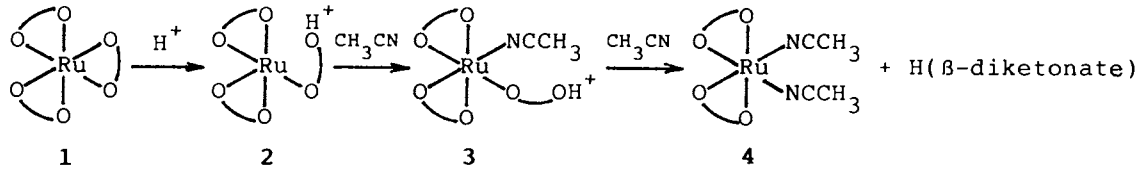

Fig. 2. Probable pathway. $\overset{O}{O}$) represents ß-diketonato ligand.

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3) $[Ru^{III}(dpm)_2(CH_3CN)_2]ClO_4$: Anal. Found: C, 49.08; H, 7.20; N, 3.98%. Calcd for $RuC_{26}H_{44}O_8N_2Cl$: C, 48.11; H, 6.83; N; 4.32%. IR (KBr) 2326, 2297 cm^{-1} (CN), 1092 cm^{-1} (ClO_4). ^1H NMR ($CDCl_3$, room temp.) δ = -91 (s, 2H, CH), 0.53 (s, 18H, $C(CH_3)_3$), 6.48 (s, 18H, $C(CH_3)_3$), 35.40 (s, 6H, CH_3CN).
4) $[Ru^{III}(acac)_2(CH_3CN)_2]ClO_4$: Anal. Found: C, 35.44; H, 4.28; N, 5.24%. Calcd for $RuC_{14}H_{20}O_8N_2Cl$: C, 34.97; H, 4.19; N, 5.83%. IR (KBr) 2324, 2295 cm^{-1} (CN), 1097 cm^{-1} (ClO_4). ^1H NMR ($CDCl_3$, room temp.) δ = -85 (s, 2H, CH), -26.93 (s, 6H, CH_3), -23.00 (s, 6H, CH_3), 37.85 (s, 6H, CH_3).
5) $[Ru^{III}(acac)(dpm)_2]$: Anal. Found: C, 57.30; H, 8.20%. Calcd for $RuC_{27}H_{45}O_6$: C, 57.20; H, 7.94%. ^1H NMR ($CDCl_3$, room temp.) δ = -40.86 (s, 2H, CH), -18.80 (s, 1H, CH), 0.92 (s, 6H, CH_3), 1.60 (s, 18H, $C(CH_3)_3$), 3.35 (s, 18H, $C(CH_3)_3$).
6) $[Ru^{III}(acac)_2(dpm)]$: Anal. Found: C, 53.34; H, 7.09%. Calcd for $RuC_{21}H_{33}O_6$: C, 52.27; H, 6.89%. ^1H NMR ($CDCl_3$, room temp.) δ = -48.06 (s, 1H, CH), -24.71 (s, 2H, CH), -4.71 (s, 6H, CH_3), -0.74 (s, 6H, CH_3), 2.54 (s, 18H, $C(CH_3)_3$).
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