A Novel Ru(II)–DMSO Complex Having Non-coordinating 1-Naphthoylamide Arm: Effects of Intramolecular Hydrogen Bonding on Redox Potential of the Ruthenium Center

Takahiko Kojima* and Yoshihisa Matsuda
Department of Chemistry, Faculty of Sciences, Kyushu University, Hakozaki, Higashi-Ku, Fukuoka 812-8581

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A Ru(II)–chloro-dimethylsulfoxide complex having tris(2-pyridylmethyl)amine with 1-naphthoylamide arm at the 6-position of one pyridyl moiety was synthesized and characterized by X-ray crystallography, spectroscopic methods, and cyclic voltammetry.

Regulation of redox potentials of metal complexes by noncovalent interactions including hydrogen bonding has been one of important issues to discuss on the control of reactivity at the metal center in the metalloenzyes. In heme proteins, axially ligating residues of amino acids form hydrogen bonding with other moieties of neighboring functional groups. As can be seen in myoglobin and horseradish peroxidase (HRP), they have common imidazole ligand on the iron centers, however, the imidazole ligand of histidine in HRP forms hydrogen bonding with aspartic acid to lower the redox potential for facilitating the formation of a high-valent Fe=O species.[1]

We have focused on Ru(II) complexes of tris(2-pyridylmethyl)amine (TPA) ligands having two amide moieties at the 6 positions of two of three pyridine rings.[2] In the case of bisamide-TPA ligands, one of amide oxygens of a ligand coordinates to the Ru(II) center and also the coordinated oxygen is linked to an N–H group of an uncoordinated amide arm by intramolecular hydrogen bonding to form stable complexes. In order to clarify the effect of the intramolecular hydrogen bonding toward coordinated amide moiety on redox properties of the Ru(II) centers, we synthesized a novel Ru(II) complex bearing a monoamide-TPA derivative with 1-naphthoylamide group.

Synthesis of a Ru(II) complex having *N*-(6-(1-naphthoyl)-amide-2-pyridylmethyl)-*N*,*N*-bis(2-pyridylmethyl)amine (1-Naph-TPA) was performed by the reaction of *cis*-$[RuCl_2(DMSO)_4]$ with *N*-(6-bis(1-naphthoyl)amide-2-pyridylmethyl)-*N*,*N*-bis(2-pyridylmethyl)amine, which was a precursor of the ligand, in ethylene glycol at 110 °C for 20 h. The reaction mixture was dried up under reduced pressure at 100 °C. A solution of $NaPF_6$ in MeOH was added to obtain a red solution and 2-propanol was added to obtain yellow-orange solids of $[RuCl(1\text{-Naph-TPA})(DMSO)]PF_6$ (**1**) (55% yield), which was washed with a mixture of MeOH/2-propanol.

A single crystal of **1**•MeOH was obtained by recrystallization from methanol solution of **1** to allow us to determine its crystal structure.[3] An ORTEP drawing of the cation moiety of **1**•MeOH is shown in Figure 1. Selected bond lengths (Å) and angles are described in the figure caption.

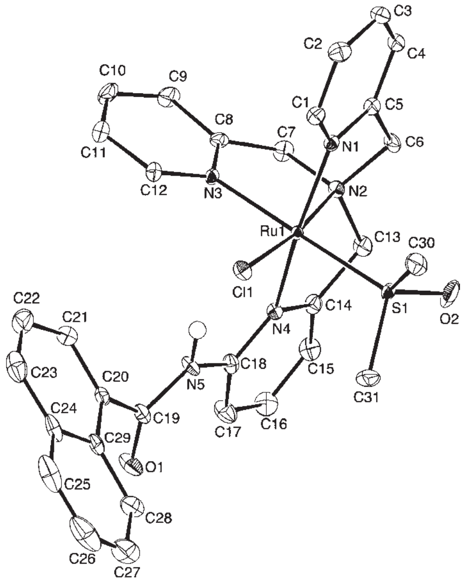
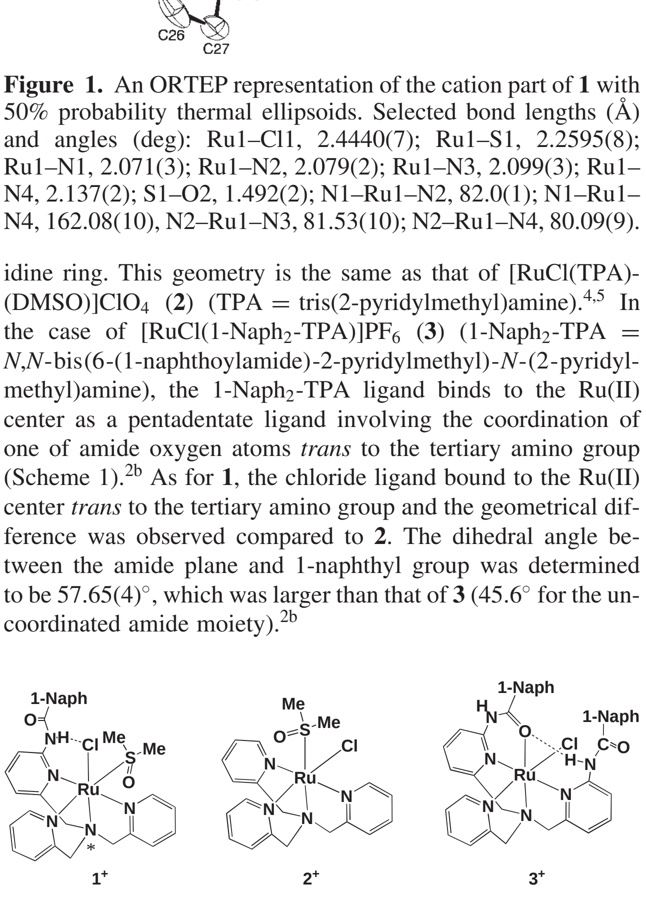


Figure 1. An ORTEP representation of the cation part of **1** with 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Ru1–Cl1, 2.4440(7); Ru1–S1, 2.2595(8); Ru1–N1, 2.071(3); Ru1–N2, 2.079(2); Ru1–N3, 2.099(3); Ru1–N4, 2.137(2); S1–O2, 1.492(2); N1–Ru1–N2, 82.0(1); N1–Ru1–N4, 162.08(10), N2–Ru1–N3, 81.53(10); N2–Ru1–N4, 80.09(9).

The complex has the TPA ligand in a tetradentate fashion, in which the pyridine ring with a 1-naphthoylamide moiety locates *trans* to a pyridine arm. The chloride anion binds to the Ru(II) center *trans* to the tertiary amino group of TPA and DMSO coordinates to the metal center with the S atom trans to one pyridine ring. This geometry is the same as that of $[RuCl(TPA)(DMSO)]ClO_4$ (**2**) (TPA = tris(2-pyridylmethyl)amine).[4,5] In the case of $[RuCl(1\text{-Naph}_2\text{-TPA})]PF_6$ (**3**) (1-$Naph_2$-TPA = *N*,*N*-bis(6-(1-naphthoylamide)-2-pyridylmethyl)-*N*-(2-pyridylmethyl)amine), the 1-$Naph_2$-TPA ligand binds to the Ru(II) center as a pentadentate ligand involving the coordination of one of amide oxygen atoms *trans* to the tertiary amino group (Scheme 1).[2b] As for **1**, the chloride ligand bound to the Ru(II) center *trans* to the tertiary amino group and the geometrical difference was observed compared to **2**. The dihedral angle between the amide plane and 1-naphthyl group was determined to be 57.65(4)°, which was larger than that of **3** (45.6° for the uncoordinated amide moiety).[2b]



Scheme 1.

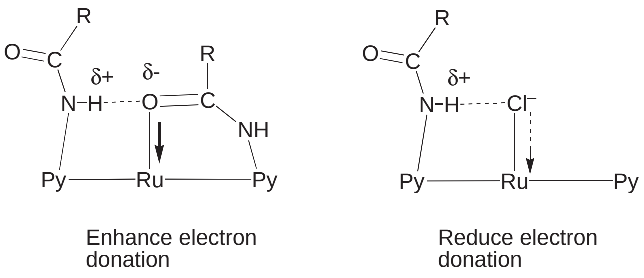
Concerning amide coordination, Masuda and co-workers have reported that Cu(II) and Ru(II) complexes bearing monopivalamide-TPA exhibit two kinds of structures, in which the amide moiety coordinates to Cu(II) or Ru(II) center or the amide N–H forms intramolecular hydrogen bonding with the proximal nitrogen of an axially bound azide anion for a Cu(II) complex.[6]

In the complex **1**, an intramolecular hydrogen bonding was observed between the chloride ligand and the N–H group of the uncoordinated amide moiety (Cl1···N5, 3.135(3) Å). IR spectrum of **1** by Nujol method showed ν(N–H) at 3122 cm^{-1}, suggesting strong hydrogen bonding.[7] This value is much lower than those of Ru(II)–bisamide-TPA complexes (3314–3335 cm^{-1}), in which the N–H moiety has been linked to the coordinated amide oxygen of the other amide part.[2b] In its ^{1}H NMR spectrum in CD_3CN, a broad singlet assigned to the N–H moiety was observed at 11.6 ppm, which exhibited a large downfield shift compared to those of **3** (ca. 10.2 ppm). This large downfield shift is consistent with the lower energy shift of ν(N–H) in the IR spectrum. VT–^{1}H NMR spectroscopy was applied to **1** in CD_3CN. The temperature dependence of N–H signal was linear with a gradient of 0.5 ppb/K, suggesting that the intramolecular hydrogen bonding should be effective even in solution.[2b]

Two singlets (3H for each) assigned to the methyl groups of DMSO ligand were observed at 2.65 and 2.97 ppm.[8] The two methyl groups of DMSO are diastereotopic in a chiral coordination environment of **1**, in which the tertiary amino nitrogen is a stereogenic center as shown in Scheme 1. In the crystal structure, the torsion angle of O2–S1–Ru1–N2 was determined to be $-5.6(1)^\circ$, indicating that the S=O bond should be almost in-plane to facilitate the π-back bonding.[4]

Cyclic voltammogram of **1** in CH_3CN (0.1 M TBAP) exhibited a reversible one electron redox wave due to a Ru(II)/Ru(III) redox couple at 0.79 V relative to ferrocene/ferrocenium as 0 V. This value is 0.18 V-higher than that of **2** (0.61 V) and 0.45 V-higher than that of **3**. In the comparison of the redox potential of **1** with that of **2**, the effect of the intramolecular hydrogen bonding is evident: The hydrogen bonding reduces the negative charge on Cl^- to weaken the electrostatic interaction between the Cl^- and the Ru(II) center and lowers the redox potential. This type of the effect on the redox potentials have been reported and discussed by Ueyama and co-workers.[9] In the comparison with **3**, the π-back bonding from the Ru(II) center to the *S*-bound DMSO ligand should be the origin of the large positive shift of the redox potential.[4]

In summary, in the Ru(II) complexes having TPA ligands with amide moiety, we have envisaged two different types of the effects of intramolecular hydrogen bonding between the coordinated atom and the uncoordinated amide N–H group on redox properties of the Ru(II) centers as shown in Scheme 2. One is to reduce the electron density of the coordinated atom of the ligand for elevating the redox potential of the Ru center. The other is to induce the negative charge on the coordinating atom of the ligand for lowering the potential. This manufacturing of the structure of the metal complexes is versatile utility toward the regulation of the redox properties of the metal center for controlling its reactivity.



Enhance electron donation

Reduce electron donation

Scheme 2.

References and Notes

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3 Crystallographic data for **1**•MeOH: Formula, $C_{32}H_{34}N_5ClSO_3PF_6Ru$; fw 829.03; monoclinic, $P2_1/n$; $a = 13.581(4)$, $b = 14.878(4)$, $c = 17.093(5)$ Å, $\beta = 90.45(2)^\circ$, $V = 3453(6)$ Å^3, $Z = 4$, $\rho = 1.594$ g cm^{-3}, μ (Mo Kα) $= 0.711$ cm^{-1}, R_1 ($I > 2\sigma(I)$) $= 0.070$, $wR = 0.187$ (all data), GOF = 1.99.

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