A Ruthenium(II)-Pyridylamine Complex Showing a Fluxional Intramolecular π–π Interaction

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A novel ruthenium(II) complex having 2-naphthoylamide groups attached to TPA (tris(2-pyridylmethyl)amine) was synthesized and characterized; the 2-naphthoylamide arms exhibited fluxional behavior of intramolecular π–π interaction.

Regulation of non-covalent interactions involving hydrogen bonding and hydrophobic π–π interaction is indispensable for efficient and reversible molecular recognition as observed in base pairing and stabilizing double helical structures in DNA.[1] As for the π–π interaction among ligands, it has been reported on Cu(II)-polypyridine-aromatic amino acid ternary complexes in which the π–π stacking interaction is apparently switched by phosphorylation and hydrolysis of the OH group of coordinated tyrosine.[2] In particular such a weak interaction as π–π interaction lies on strong geometrical requirements for interactions.[3] Thus, an intra- or intermolecular π–π interaction can be controlled in a topological alteration of aromatic moieties in molecules.

In the course of our research on ruthenium–TPA (TPA = tris(2-pyridylmethyl)amine) complexes,[4] we started to synthesize a new series of complexes having certain functionality on the TPA ligand to generate novel working devices toward molecular recognition. Thus, as an initial attempt for the development of functional molecular devices based on a ruthenium–TPA complex, we introduced naphthoylamide groups to TPA aiming at the hydrophobic π–π interaction as a driving force of recognition. We report herein synthesis and characterization of a novel Ru(II)–TPA complex having two 2-naphthoylamide moieties which was revealed to perform thermal regulation of intramolecular π–π interaction.

The complex, $[\mathrm{RuCl}((2\text{-naph})_2\text{–TPA})]\mathrm{PF}_6$ (**1**) ($(2\text{-naph})_2$–TPA = bis(6,6'-(2-naphthoylamido)-2,2'-pyridylmethyl)-(2-pyridylmethyl)amine) was synthesized as follows:[5] a mixture of $\mathrm{RuCl_3{\cdot}3H_2O}$ with $(2\text{-naph})_4$-TPA (bis(6,6'-bis(2-naphthoyl)amido)-2,2'-pyridylmethyl)(2-pyridylmethyl)amine) in ethanol was refluxed for 24 h. In this process, were observed the solvolysis of the tetraamide to form the diamide ligand and the reduction of Ru(III) to Ru(II) as a result.

The crystal structure of **1** was determined by X-ray crystallography.[6] Its ORTEP drawing is depicted in Figure 1 with selected bond lengths and angles in the caption. As can be seen in the figure, $(2\text{-naph})_2$–TPA ligand bound to Ru(II) center as a pentadentate ligand including an amide oxygen of one of the 2-naphthoylamide moieties. The coordinated amide C=O group was interacted with the N–H of the uncoordinated naphthoylamide arm via an intramolecular hydrogen bonding (2.978(3) Å). For the two 2-naphthyl groups, the nearest separation were 3.395(5) Å for C(27)···C(38) and followed by 3.458(5) Å for C(27)···C(31), 3.494(5) Å for C(26)···C(39), indicating an intramolecular π–π interaction between them. The separation between the centers of two naphthalene rings was estimated to be 4.51 Å. In this complex, the π–π interaction is not "face-to-face" but getting closer to a "T-shaped" geometry; the two 2-naphthyl groups were not cofacial and had a dihedral angle of 27.3°. Dihedral angles of 6-(2-naphthoylamide)pyridyl moieties were calculated to be 10.4° and 20.9° for pyridine–amide planes in coordinated and uncoordinated ones, respectively, and 20.3° and 19.9° for amide–naphthalene planes in the same manner, indicating higher planarity of the coordinated amide.

Bond lengths among the ruthenium center and pyridine rings were deviated from 2.115(3) Å for Ru1–N(4) to 2.009(3) Å for Ru1–N(3) in **1**. Such difference among Ru–pyridine nitrogen bond lengths has not been observed for other Ru–TPA complexes characterized by X-ray crystallography.[4b,d] The shortest bond length of Ru–N(3) in **1**, which involves the pyridine ring connected to the coordinated amide moiety, is attributable to the expansion of conjugated π-system from the pyridine to the coordinated amide which lowers the energy level of its π* orbitals to facilitate π-back bonding interaction from Ru dπ orbitals. In addition, the coordination of the amide C=O moiety is strengthened by π-back bonding from the Ru dπ orbital to pπ* orbital of the C=O bond and this results in the elongation of the C=O bond.

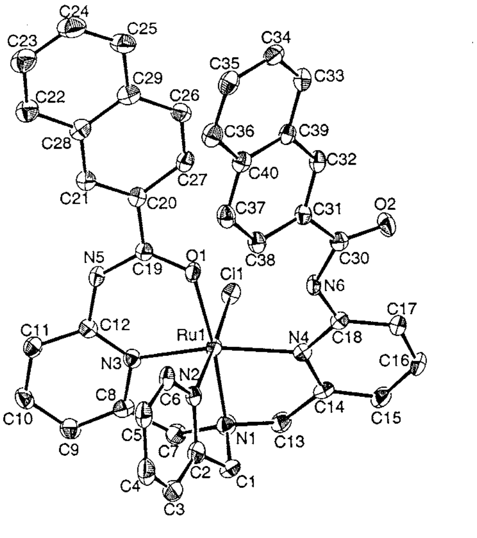


Figure 1. An ORTEP drawing of **1** (cation moiety, 50% probability thermal ellipsoids, H atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): Ru1-Cl1, 2.436(1); Ru1-O1, 2.107(3); Ru1-N1, 2.053(3); Ru1-N2, 2.057(3); Ru1-N3, 2.009(3); Ru1-N4, 2.115(3); O1-C19, 1.263(4); O2-C30, 1.223(4); O1-Ru1-N3, 89.8(1); N1-Ru1-N2, 82.3(1); N1-Ru1-N3, 85.6(1); N1-Ru1-N4, 79.9(1); Cl1-Ru1-N2, 175.51(9); O1-Ru1-N1, 174.1(1); N3-Ru1-N4, 164.6(1); O1-C19-N5, 124.0(3); O1-C19-C20, 119.0(3); N5-C19-C20, 117.0(3).

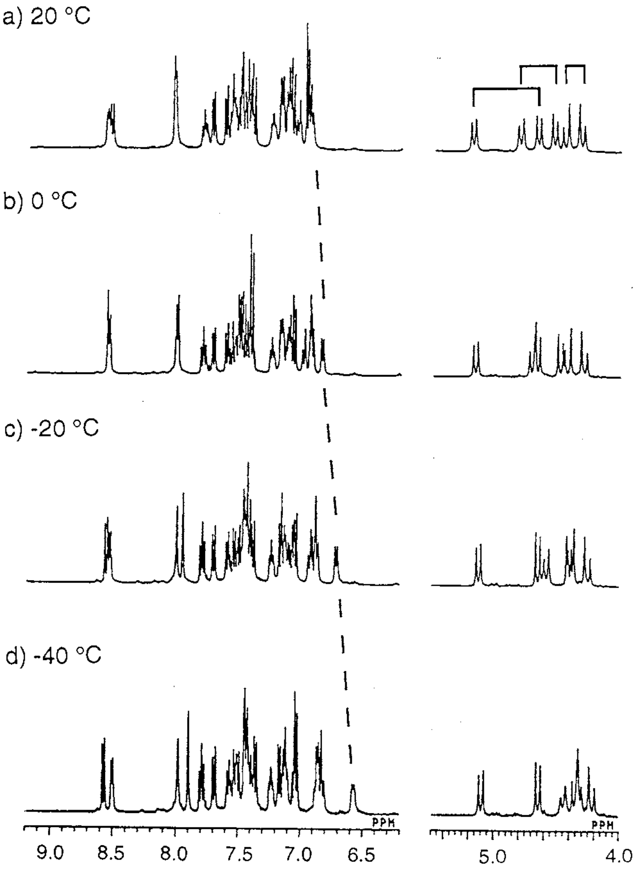
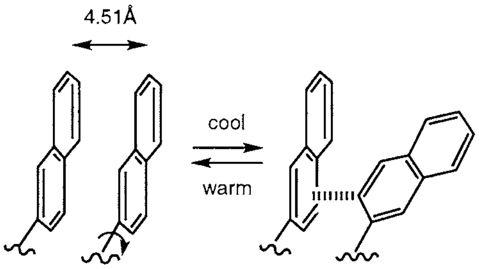


Figure 2. Variable temperature ^{1}H-NMR (400MHz) spectra of **1** in CD_3CN.



Scheme 1. Schematic description of thermal motion of 2-naphthyl groups in **1**.

In the ^{1}H NMR spectrum (400MHz) of **1** in CD_3CN, three AB quartets assigned to the methylene protons were observed; 4.27 and 4.52 ppm (J_{AB} = 18 Hz), 4.49 and 4.98 ppm (J_{AB}= 15Hz), and 4.66 and 5.20 (J_{AB}= 14 Hz). This is indicative of the fact that the amide C=O moiety is bound to the ruthenium center to hold an asymmetric coordination environment even in a solution. As for signals due to methylene protons of tetradentate TPA derivatives coordinated to Ru(II) centers, they have been observed as one singlet and one AB quartet in a similar region due to one symmetrical plane.[4b] Signals due to N–H groups were observed at 10.33 and 10.46 ppm for **1** as broad singlets. Concerning resonances attributable to aromatic protons, peak assignments were unsuccessful because of their severe overlap.

In order to shed some lights on the solution behavior of the complex, variable temperature ^{1}H NMR spectroscopy was applied to their CD_3CN solutions in the range from –40 to 20 °C (Figure 2). Of our interest, it was revealed that the intramolecular π–π interaction in **1** was able to perform thermal fluxional behavior as proposed in Scheme 1. As can be seen in Figure 2, upfield shifts due to dynamic motion of the naphthyl groups were observed around aromatic region. At lower temperatures, the interaction was evidenced by an upfield shift of a doublet at 6.57 ppm (–40°C) assignable to probably the 3-H of a naphthyl group. The chemical shifts of several peaks showed linear relationships to 1/T, indicating the mode of fluxional behavior of the intramolecular π–π interaction should be unique. Thermodynamic parameters for the interaction was estimated to be $\Delta H° = -2.3$ kJ·mol^{-1}, therefore, $\Delta G° = -0.9$ kJ·mol^{-1} and $\Delta S° = -7.7$ J·mol^{-1}·K^{-1} at –40 °C.[7]

In summary, we synthesized and characterized a novel ruthenium(II)–TPA complex with a functional group to exhibit a thermal and fluxional behavior for an intramolecular π–π interaction. Functionality of this and related ruthenium complexes is under investigation.

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References and Notes.

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5 Yield; 71 %. Anal. Calcd for $C_{40}H_{32}N_6O_2ClRuPF_6 \cdot H_2O$: C, 51.75; H, 3.69; N, 9.05. Found: C, 51.53; H, 3.59; N, 9.22. Absorption maxima (λ_{max}, ε (mol^{-1}·L·cm^{-1})) in CH_3CN: 426 nm (br), 8.4×10^3; 280 nm, 3.7×10^4. Cyclic voltammogram data of **1** in CH_3CN (25 °C, 0.1 M of $[(n\text{-butyl})_4N]ClO_4$ as an electrolyte): +0.30 V relative to ferrocene/ferricinium couple as 0 V. Utilization of $(2\text{-naph})_4$–TPA was preferred to that of $(2\text{-naph})_2$–TPA due to much easier purification of the tetraamide than the diamide.

6 $\mathbf{1} \cdot H_2O \cdot 1/2C_2H_5OH$; formula $C_{41}H_{37}N_6O_{3.5}F_6ClPRu$, M = 951.27, triclinic, $P\bar{1}$, a = 13.3675(5), b = 14.3432(7), c = 10.0746(6), α = 98.118(2), β = 93.159(3)°, γ = 92.832(2)°, V = 1906.2(2) Å^3, Z = 2, D_{calcd} = 1.657 g/cm^3, μ (Mo Kα) = 6.05 cm^{-1}, T = –170 °C, R (Rw) = 0.040 (0.056) for 6033 reflections ($I > 3\sigma(I)$).

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