



A ruthenium(II) complex having a ligand undergoing partial C = N cleavage and unusual double-bond shift and nonchirality



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ABSTRACT

A novel six-coordinate ruthenium(II) complex **1**, formulated as $[\text{Ru}(\text{bpy})_2\text{L}_b]\text{PF}_6 \cdot \text{C}_2\text{H}_5\text{OH}$ (bpy = 2,2'-bipyridine), has been obtained and characterized. Ligand L_b in **1** comes from a chiral bis-Schiff-base ligand L_a which is condensed between sodium(I) salt of D- or L-phenylalanine and terephthalaldehyde. It is noted that ligand L_a undergoes partial C = N bond cleavage of Schiff-base unit forming a free aldehyde group at one end of phenyl ring, and an unusual proton migration, a C = N double-bond shift and subsequent nonchirality at the other end simultaneously in the presence of a ruthenium(II) ion.

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Investigations on the α -amino acids and their derivatives have attracted much attention because syntheses, structures, reactions, and applications of these compounds are important in many research fields such as biochemistry, organic and organometallic chemistry [1–4]. Schiff bases having chiral α -amino acid units and their metal complexes and metalloproteins can afford useful candidates on the therapeutic pharmaceuticals of malignant tumor [5,6].

However, the Schiff-base unit is not chemically stable because of the reversible formation and cleavage of C = N double bond. We have previously reported a series of enantiomeric and racemic Schiff-base macrocyclic ligands with different cadmium(II), zinc(II), manganese(II), nickel(II) and copper(II) salts undergoing the cleavage of Schiff-base imine double bonds and subsequent ring contraction of the macrocyclic ligands due to the size effects and the spatial restrictions of coordination geometry of the central metals, the steric hindrance of ligands and the counterions used [7–11].

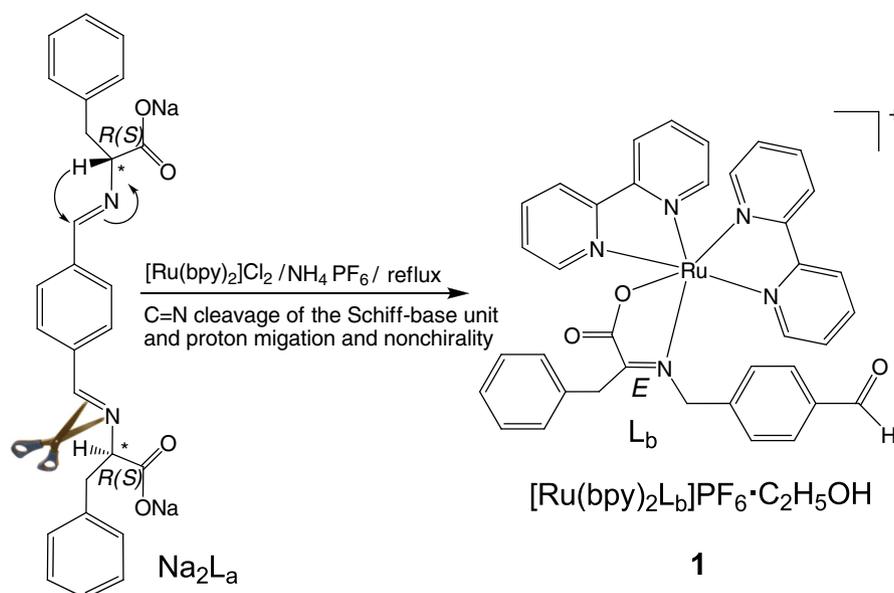
In our previous study, an enantiomeric pair of sodium(I) directed organic/inorganic frameworks formulated $[\text{Na}_4(\text{H}_2\text{O})_{12}]_n \cdot [2\text{L}_a]_n$ has been described, where ligand L_a is condensed between sodium(I) salt of D- or L-phenylalanine and terephthalaldehyde [12]. To further explore their coordination chemistry, a Ru(II) ion is used to react with this enantiomeric pair of chiral ligands and herein we report an unexpected example of novel ruthenium(II) complex $[\text{Ru}(\text{bpy})_2\text{L}_b]\text{PF}_6 \cdot \text{C}_2\text{H}_5\text{OH}$ (**1**) where ligand L_b derives from partial C = N cleavage of Schiff-base unit and proton migration, double-bond shift and subsequent nonchirality at both ends of ligand L_a at the same time. Actually, the cleavage of Schiff-base unit in L_a is easy to be understood as we

mentioned above. Nevertheless, the study is unusual in literature on the proton migration and subsequent C = N double-bond shift in the presence of a metal ion, which will make the resultant ligand nonchiral.

Complex **1** can be obtained by refluxing equal molar ratio of Na_2L_a and $[\text{RuCl}_2(\text{bpy})_2] \cdot \text{H}_2\text{O}$ in methanol and adding an excess saturated aqueous solution of NH_4PF_6 [13]. Here a new ligand L_b has been yielded in Ru(II) complex **1** where partial C = N cleavage of chiral bis-Schiff-base ligands and subsequent double-bond shift and racemization take place (Scheme 1). In our experiments, each of sodium(I) salt of bis-Schiff-base ligand, condensed between D- or L-phenylalanine and terephthalaldehyde, produces the same achiral ligand L_b . Electrospray ionization mass spectrum (ESI-MS) of complex **1** in the positive ion mode gives a most intense peak centered at $m/z = 694.17$ (calculated: 694.14), as can be seen in Fig. 1, which is assigned to the monovalent cationic peak of $([\text{Ru}(\text{bpy})_2\text{L}_b]^+)$ in complex **1**. Furthermore, the isotopic distributions of $[\text{Ru}(\text{bpy})_2\text{L}_b]^+$ cation at 100% abundance are calculated by using the numbers and natural isotopic abundance of atoms and the results are in good agreement with the experimental data (the Inset of Fig. 1), indicative of the existence of expected $[\text{Ru}(\text{bpy})_2\text{L}_b]^+$ species.

In addition to the strong C = N Schiff-base absorption at 1638 cm^{-1} , Fourier transform infrared (FT-IR) spectrum of complex **1** reveals the presence of two new peaks at 1686 and 841 cm^{-1} , corresponding to the characteristic absorptions of free aromatic aldehyde group of L_b after partial C = N cleavage of bis-Schiff-base ligands and hexafluorophosphate anion. Compared with the electronic spectrum of compound Na_2L_1 [12], the strong absorption peak at 293 nm in complex **1**, which corresponds to the $\pi-\pi^*$ transition of the azomethine chromophore, exhibits a bathochromic shift of 12 nm after the degradation and proton migration of ligand L_a . Furthermore, a new broad

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Scheme 1. Schematic illustration of the preparation of Ru(II) complex **1** where the chiral carbon atoms are marked with asterisks.

absorption band centered at 481 nm in complex **1** is found, which can be assigned to the typical metal-to-ligand charge transfer after the Ru(II) ion complexation. Moreover, the single-crystal structure of complex **1** has been successfully obtained by using the X-ray diffraction method, which will be discussed below.

X-ray single-crystal structural analyses of complex **1** [14] reveal that the coordination geometry for the six-coordinate Ru(II) center is a distorted octahedron with the Ru–O distance of 2.083(5) Å and Ru–N distances ranging from 2.024(6) to 2.049(6) Å, as illustrated in Fig. 2. Ligand L_b exhibits *E* configuration in complex **1** and its carboxylic group

adopts a monodentate coordination fashion with the central Ru(II) ion. Compared with the bis-Schiff-base ligand L_a , partial cleavage of C = N double bond occurs and an aldehyde group is uncoordinated with the O3–C37 double bond length of 1.251(13) Å. The dihedral angle between the two bpy planes in complex **1** is 87.1(2)°, while that between the two phenyl rings in ligand L_b is 60.0(2)°. In addition, the dihedral angle between one of the bpy ligands and the benzaldehyde plane in ligand L_b is 9.4(2)°, where intramolecular π – π stacking interactions are found between one pyridine ring of this bpy ligand and the phenyl ring with the centroid-to-centroid separation of 3.650 Å.

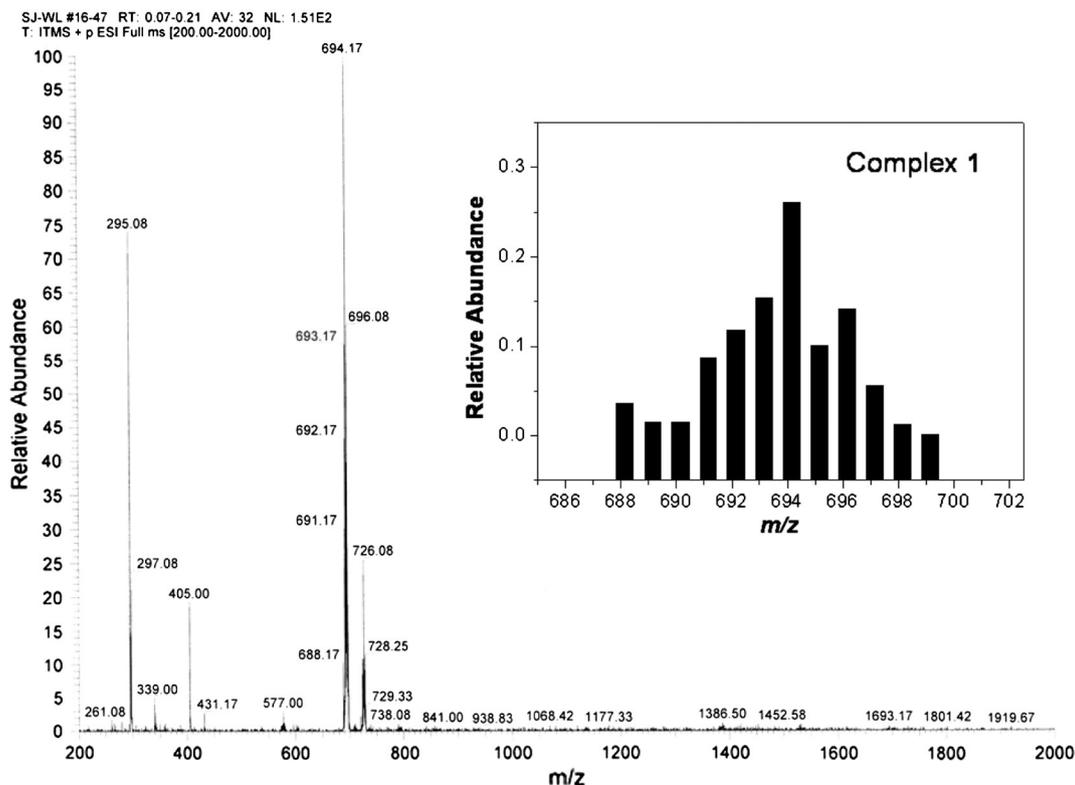


Fig. 1. Positive ESI-MS spectrum of Ru(II) complex **1** obtained in the positive mode, together with the calculated IDPs (Inset) corresponding to the peak at 100% abundance for comparison.

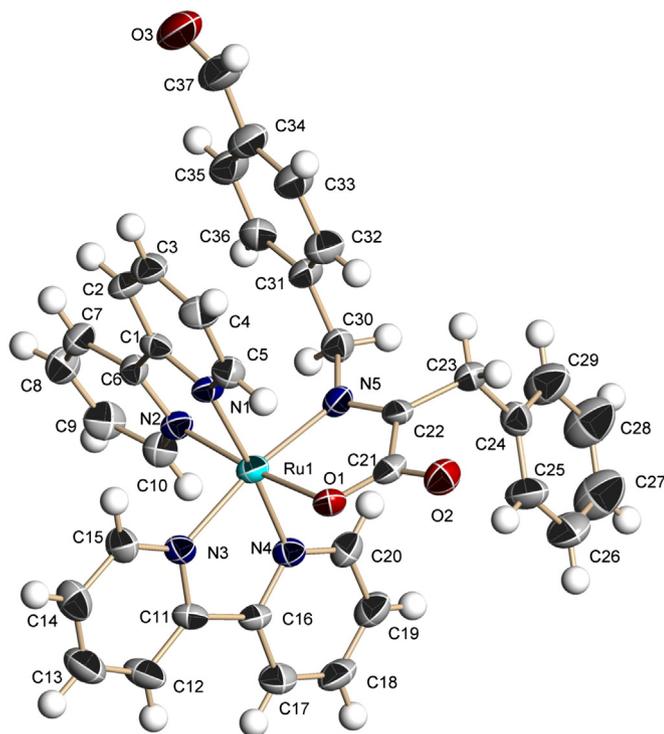


Fig. 2. ORTEP diagram (30% thermal probability level ellipsoids) of the cationic structure of Ru(II) complex **1** with the atom-numbering scheme. Selected bond lengths and bond angles (Å and °): Ru1–O1, 2.083(5), Ru1–N1, 2.046(6), Ru1–N2, 2.034(6), Ru1–N3, 2.026(6), Ru1–N4, 2.049(6), Ru1–N5, 2.024(6), N5–C30, 1.433(9), N5–C22, 1.293(10), C21–C22, 1.526(11), C22–C23, 1.496(10), O1–C21, 1.250(9), O2–C21, 1.253(9), O3–C37, 1.251(13) Å; O1–Ru1–N1, 94.7(2), O1–Ru1–N2, 173.4(2), O1–Ru1–N3, 94.0(2), O1–Ru1–N4, 88.0(2), O1–Ru1–N5, 78.9(2), N1–Ru1–N2, 79.2(2), N1–Ru1–N3, 97.5(2), N1–Ru1–N4, 175.4(2), N1–Ru1–N5, 89.2(2), N2–Ru1–N3, 89.3(2), N2–Ru1–N4, 98.3(2), N2–Ru1–N5, 98.3(2), N3–Ru1–N4, 78.5(2), N3–Ru1–N5, 170.7(2), N4–Ru1–N5, 95.1(2)°.

Furthermore, typical intermolecular π – π stacking interactions are found between adjacent two molecules forming a dimeric packing structure in complex **1** with the centroid-to-centroid separation of 3.897 Å (Fig. 3).

It is very interesting to mention that an unusual proton migration is found to occur from the stereogenic carbon atom of the phenylalanine component to the carbon atom of the imine moiety (Scheme 1). The proton migration in the course of the Ru(II) complexation is suggested to cause the shift of a C = N double bond, as indicated by the related

bond lengths in complex **1**, and subsequent loss of the chirality of L_b . Compared with the N–C and C = N bond lengths in the starting material Na_2L_a , where 1.456(6)–1.467(6) Å for the single bond (phenylalanine moiety) and 1.253(6)–1.269(6) Å for the double bond (Schiff-base moiety) are observed, the N5–C30 and N5–C22 bond lengths in complex **1** are 1.433(9) and 1.293(10) Å, respectively, indicative of typical single-bond and double-bond character.

So a unique rearrangement of a Schiff-base ligand in a Ru(II) coordination sphere takes place involving the proton migration to cause the shift of a C = N double bond in ligand L_b , which is accompanied by the disappearance of a chiral center (C22) in this case. Moreover, the crystallization of complex **1** in a centrosymmetric triclinic space group $P\bar{1}$ can also be regarded as an evidence for the disappearance of chirality for ligand L_b . In contrast, the two C–O and C = O bond lengths of carboxylic unit in complex **1** are 1.250(9) Å for the coordinated one and 1.253(9) Å for the free one, which lie within the range of 1.228(7)–1.264(6) Å in the starting material of Na_2L_a .

Thus far, investigations on the hydrogen migration and subsequent double-bond shift and racemization of a chiral ligand are very rare in literature. Nevertheless, there has been considerable interest in the oxidative dehydrogenation of coordinated amines to the corresponding imines or nitrile in the presence of certain Ru(II) complexes [15–20]. It is already known that imines of α -amino ester exist in solution in the tautomeric equilibrium with corresponding azomethine ylides [21], which would make possible the proton migration in this case. Furthermore, the electron transfer from the coordination nitrogen atom of Schiff-base unit to the Ru(II) center after metal–ligand coordination interactions is suggested to play important roles in the cleavage of Schiff-base C = N double at one end as well as the proton migration at the other end of ligand.

In summary, we report herein a novel six-coordinate ruthenium(II) complex **1**, formulated as $[Ru(bpy)_2L_b]PF_6 \cdot C_2H_5OH$, where a unique nonchiral ligand L_b is formed from a chiral bis-Schiff-base ligand with two stereogenic centers derived from D- or L-phenylalanine. In the process of Ru(II) ion complexation, the enantiomeric ligands undergo half C = N cleavage of Schiff-base unit forming a free aldehyde group at one end, and at the same time, an unusual proton migration and a following C = N double-bond shift take place at the other end making the L_b ligand nonchiral. Moreover, typical intramolecular π – π stacking interactions are found between adjacent bpy and phenyl rings in complex **1** with the centroid-to-centroid separation of 3.650 Å, and a dimeric packing structure is formed between the aromatic rings of neighboring molecules with the centroid-to-centroid separation of 3.897 Å.

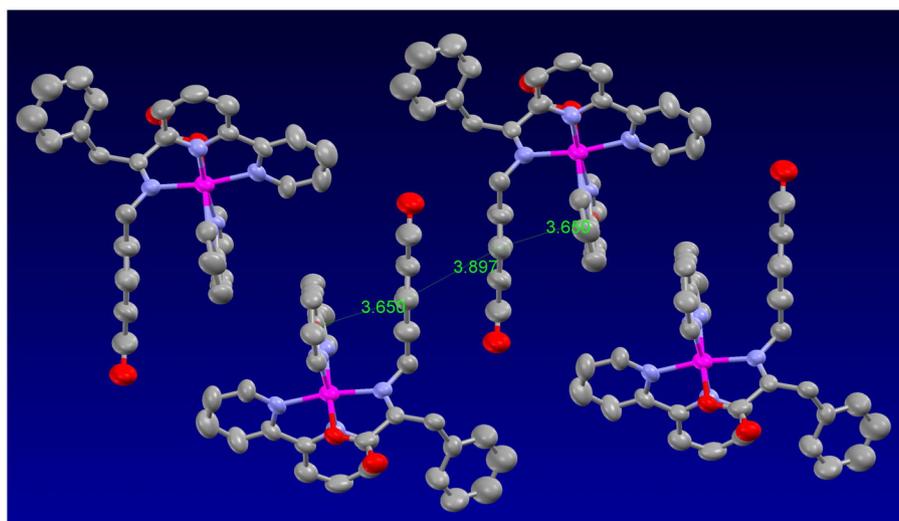


Fig. 3. Perspective view of the dimeric packing structure in Ru(II) complex **1**. Hydrogen atoms, anions and solvent ethanol molecules are omitted for clarity.

Acknowledgments

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- [12] L. Wang, W. Huang, Z.L. Chu, S.H. Gou, *Inorg. Chem. Commun.* 12 (2009) 4–7.
- [13] Preparation of complex **1**: A solution of Na_2L_a (0.047 g, 0.100 mmol) in methanol (20 cm^3) was added to a solution of *cis*-bis(2,2'-bipyridine)dichlororuthenium(II) hydrate (0.048 g, 0.100 mmol) in 80 cm^3 methanol. This mixture was refluxed for 4 h and then an excess saturated aqueous NH_4PF_6 solution was added. The resulting mixture was refluxed for additional 0.5 h, cooled to room temperature and filtered. The deep-red single crystals of **1** suitable for X-ray diffraction determination were obtained by slow evaporation of the filtrate for six days at room temperature in air with a yield of ~23%. Main FT-IR (KBr pellets, cm^{-1}): 3415 (s), 1686 (m), 1638 (s), 1495 (m), 1463 (m), 1446 (m), 1421 (m), 841 (vs), 765 (m) and 558 (m). Elemental Analysis: calculated for $\text{RuC}_{39}\text{H}_{36}\text{N}_5\text{O}_4\text{PF}_6$ (884.77): C, 52.94; H, 4.10; N, 7.92. Found: C, 53.08; H, 4.31; N, 7.84. Positive ESI-MS: $m/z = 694.17$ (calculated: 694.14) $[\text{Ru}(\text{bpy})_2\text{L}_a]^+$ (100%). UV-Vis (λ_{max} in methanol): 481 and 293 nm
- [14] Single-crystal sample of complex **1** was glue-covered and mounted on the top of a glass fiber and used for data collection on a Bruker SMART 1 K CCD diffractometer at 291(2) K using graphite mono-chromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The collected diffraction data were reduced by using the SAINT program and empirical absorption corrections were done by using the SADABS program. Both of the structures were solved by direct method and refined by least-squares method on F_o^2 by using the SHELXTL-PC software package. All non-H atoms were anisotropically refined and all hydrogen atoms were inserted in the calculated positions assigned fixed isotropic thermal parameters and allowed to ride on their respective parent atoms. Crystallographic data for $\text{RuC}_{39}\text{H}_{36}\text{N}_5\text{O}_4\text{PF}_6$: $M = 884.77 \text{ g/mol}$, crystal size, $0.10 \times 0.10 \times 0.10 \text{ mm}$, crystal system, triclinic, space group $P\bar{1}$ (No. 2), $a = 9.7749(16)$, $b = 13.770(2)$, $c = 14.138(2) \text{ \AA}$, $\alpha = 96.192(3)$, $\beta = 95.220(2)$, $\gamma = 93.772(3)^\circ$, $V = 1878.5(5) \text{ \AA}^3$, $Z = 2$, $D_c = 1.564 \text{ g/cm}^3$, $\mu = 0.539 \text{ mm}^{-1}$, $F(000) = 900$, parameters = 499, restraints = 0, $S = 0.806$. $R_1 = 0.0637$, $wR_2 = 0.0991$ for 2456 observed [$I > 2\sigma(I)$] data, $R_1 = 0.1515$, $wR_2 = 0.1151$ for all 6543 data, and max./min. $\Delta\rho = 0.514 / -0.555 \text{ e \AA}^{-3}$. There are only four C type errors in the CIF checking file about large ellipsoids for three aromatic carbon atoms and one aldehyde carbon atom because of the low quality diffraction data of single-crystal sample (38% ratio of observed/unique reflections), so no restraint was used in this case to refine the structure of complex **1**
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