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From Eilatin to Isoeilatin: A Skeletal Rearrangement Strongly Influences π-Stacking of Ru(II) Complex

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The C_1-symmetrical complex $[Ru(bpy)_2(ieil)][PF_6]_2$ exhibits unique electrochemical and photophysical properties, and forms discrete dimers in solution and in the solid state held by weak $\pi-\pi$ stacking interactions via its isoeilatin ligand, preferentially from one of its faces and in a specific orientation.

Group VIII polypyridyl complexes have attracted considerable attention due to their photophysical behavior.[1,2] Employing extended fused aromatic ligands may, on one hand, allow the fine-tuning of this behavior and, on the other hand, lead to aggregation of these complexes via $\pi-\pi$ stacking interactions. Recently, we explored Ru(II) and Os(II) complexes of eilatin-type ligands, all of which possess a large fused aromatic surface.[3,4] These complexes were found to exhibit interesting electrochemical and photophysical properties, formation of discrete dimers in solution and in the solid state held together by $\pi-\pi$ stacking interactions,[4−6] as well as anti-HIV activity,[7] and interaction with DNA.[8] Isoeilatin (**1**) is a structural isomer of eilatin (Figure 1)[9] that has never been studied as a ligand before. In this work we aimed to reveal the effect of this skeletal rearrangement on the properties of the complex and, especially, compare its stacking behavior to that of the eilatin complex that features the same aromatic surface area.

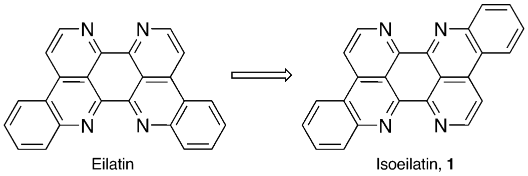

Figure 1. Structures of eilatin (left) and isoeilatin (**1**).

We synthesized **1** according to the methodology developed by Kashman and co-workers[9] and prepared the complex $[Ru(bpy)_2(ieil)][PF_6]_2$ (**2**) in its racemic form by reacting *rac*-*cis*-$[Ru(bpy)_2Cl_2]$ with 1 equiv of **1** in ethylene glycol at 100 °C for 8 h. The dark green complex was purified by chromatography and isolated as the PF_6^- salt in an overall yield of 51%. The NMR spectrum in CD_3CN, FAB-MS, and elemental analysis all indicated that complex **2** was mononuclear (see Supporting Information).

The absorption spectrum of **2** in acetonitrile is similar to that of the related eilatin complex $[Ru(bpy)_2(eil)][PF_6]_2$ (**3**),[3,5] the most prominent feature being an exceptionally low energy band around 593 nm, assigned to a $d_\pi(Ru) \rightarrow \pi^*(ieil)$ MLCT absorption. The redox behavior of **2** in acetonitrile also resembles that of **3**,[6] namely, a reversible $Ru^{II/III}$ oxidation wave appearing at 1.42 V vs SCE, and a highly facile reversible first reduction wave at −0.40 V vs SCE, which is attributed to the reduction of the isoeilatin ligand (see Supporting Information).

We expected that the isoeilatin complex **2** would exhibit stacking similar to that of the analogous eilatin complex **3**, namely, formation of discrete dimers with roughly the same dimerization constant.[5] Indeed, the ^1H NMR spectra of complex **2** in CD_3CN change as a function of concentration and temperature due to this phenomenon, and the isoeilatin protons exhibit downfield shifts reaching up to 0.81 ppm upon dilution in the concentration range 1−10 mM. However, this shifting corresponds to a dimerization constant of only 34 ± 5 M^{-1} at 297.3 ± 0.1 K, which is an order of magnitude lower than that observed for **3**.[5]

To further support this unexpected discrepancy between the eilatin and the isoeilatin complexes we conducted diffusion NMR experiments[10−12] of these two complexes in the concentration range of 1.0−10.0 mM (see Supporting Information), which led to the following findings: (a) The diffusion coefficients of both **2** and **3** increase upon dilution

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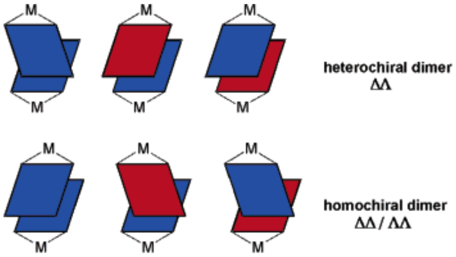

Figure 2. Schematic representation of the various dimers that may form as a result of π-stacking via the isoeilatin moiety. Upper row: heterochiral dimers, composed of two complex molecules of opposite chirality (ΔΛ). Bottom row: homochiral dimers, composed of two complex molecules of identical chirality (ΔΔ or ΛΛ). The red and blue colors represent the two different faces of the complexed isoeilatin.

as expected for systems exhibiting self-aggregation phenomena. (b) Although these complexes are of the same molecular weight and similar shape, the diffusion coefficient of **3** is lower than that of **2** in each concentration, supporting a weaker aggregation of **2**. (c) The diffusion data best fit a dimerization process rather than higher order aggregation.[13] (d) The dimerization constant of **2** is estimated to be ca. 1 order of magnitude lower than that of **3**. These results are in good agreement with the results obtained by the chemical shift variation method.

Complex **2** can form six different dimers in solution as illustrated in Figure 2. The different forms arise from both the homo-/heterochiral variation and the two different faces of the complexed isoeilatin ligands, as **2** is of C_1 symmetry. Notably, half of these forms lead to enhanced long axis vis-à-vis long axis overlap, and half to reduced long axis vis-à-vis short axis overlap (the long axis corresponds to the five ring diagonal, and the short axis to the three ring diagonal). Of the four bpy H^6 protons in complex **2**, two are outside the effective overlap area, so their chemical shifts are not expected to be affected by stacking. The remaining two are close to the isoeilatin surface, each pointing toward a different face. Significantly, only one of those H^6 protons exhibits concentration induced shifting (Figure 3), suggesting that π-stacking preferentially occurs through a specific face. These observations are supported by NOE correlations (see Supporting Information).

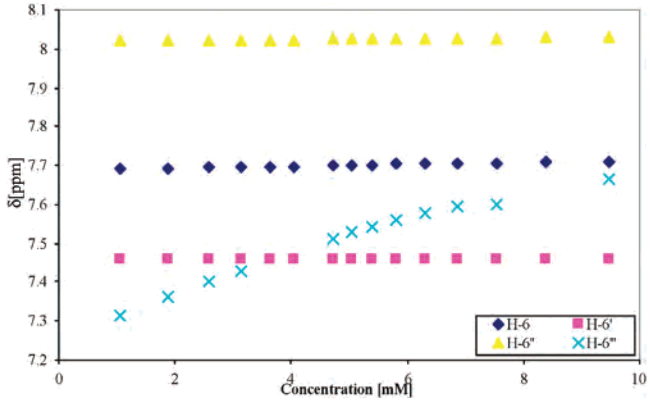

Figure 3. Variation of the chemical shifts of the four bpy H^6 protons of $[Ru(bpy)_2(ieil)][PF_6]_2$ (**2**) as a function of concentration. Only one proton exhibits a marked shift.

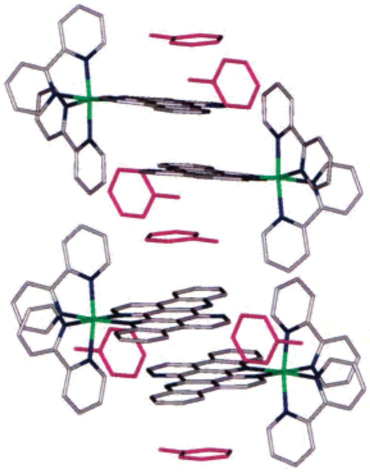

Figure 4. Crystal packing of $[Ru(bpy)_2(ieil)][PF_6]_2$ (**2**), exhibiting π-stacking between isoeilatin ligands in the two distinct dimer units, and between the dimers and toluene molecules. Counterions and acetonitrile solvent molecules omitted for clarity.

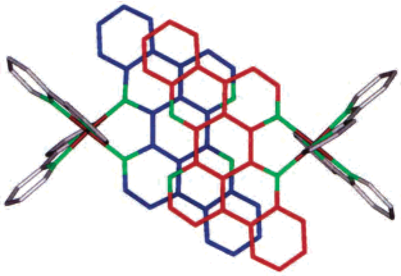

Figure 5. Crystal packing of $[Ru(bpy)_2(ieil)]Cl_2$ (**4**), exhibiting π-stacking between isoeilatin ligands in the dimer. Counterions and solvent molecules omitted for clarity.

To gain further information on the preferred dimerization mode, we grew single crystals of **2** from a CH_3CN/toluene mixture and solved its X-ray structure. The crystal lattice consists of discrete heterochiral dimers of **2**, held together by significant face-to-face π-stacking interactions via the

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(12) Characterization of self-association processes by diffusion NMR is qualitative since both monomer and aggregate exist in each concentration, thus it is nearly impossible to measure the diffusion coefficient of the isolated monomer. See, for example: (a) Proudfoot, E. M.; Mackay, J. P.; Karuso, P. *Dalton Trans*. **2003**, 165. (b) Macchioni, A.; Romani, A.; Zuccaccia, C.; Guglielmetti, G.; Querci, C. *Organometallics* **2003**, *22*, 1526.

(13) The ratio between the diffusion coefficient of a 1.0 mM solution of **2** (presumably mostly monomers) and 10.0 mM solution of **3** (presumably mostly aggregates) is 1.25 ± 0.03, consistent with a dimerization process.[11c]

(14) Two distinct dimers are apparent in the unit cell, in which the nearly planar aromatic frameworks of the isoeilatin partly overlap each other. The mean distances between the overlapping delocalized segments are 3.42 and 3.36 Å, indicating significant interaction between them. Two types of toluene molecules are apparent in the crystal lattice. The paired complexes and one of the toluene species parallel stack in an alternating manner, the intercalated toluene lying at an average distance of 3.55 Å from the molecular surface of one pair and 3.60 Å from the other pair, suggesting further stabilization of the structure by stacking interactions. The second toluene species is located between adjacent columns approaching in a nearly perpendicular fashion to one of the isoeilatin frameworks.

isoeilatin moiety[14] (Figure 4). In the dimer, the isoeilatin ligands are oriented long axis vis-à-vis long axis, and dimerization occurs through only one particular isoeilatin face. Significantly, this stacked-dimer pattern persists even upon changing the counterion to Cl^- and the crystallization solvent system to MeOH/ether (complex **4**, Figure 5).[15]

On the basis of the repeating pattern in the solid state, and the assumption that π-stacking preferentially occurs over the largest possible area, we propose that, in solution, the complex forms π-stacked dimers arranged long axis vis-à-vis long axis via their isoeilatin units. NMR data has indicated that dimerization occurs via a specific face. An examination of Figure 2 leads to the conclusion that the preferred dimer is a heterochiral one, as homochiral dimers do not allow a combination of long axis vis-à-vis long axis via a specific face. Thus, although all six possible dimers are probably in fast equilibrium in solution, only one of them is strongly favored, i.e., the isoeilatin ligand exhibits *face-selective* dimerization.

In conclusion, we have demonstrated that the electronic properties of isoeilatin are closely related to those of eilatin, whereas, unexpectedly, the stacking tendencies diverge significantly. We are currently exploring the source of this discrepancy and its possible application.

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Supporting Information Available: CIFs of **2** and **4**, experimental preparations, and full characterization of the compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) The mean distance between the overlapping delocalized segments of the isoeilatin in **4** is 3.36 Å, indicating significant interaction between them.