Ruthenium complexes of eilatin: face selectivity in octahedral geometry; synthesis of $[Ru(bpy)_2(eilatin)]^{2+}$ and $[Ru(phen)_2(eilatin)]^{2+}$

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Eilatin, a marine alkaloid, is a potentially bifacial ligand that prefers to bind through its less hindered face in sterically demanding geometries as evident by the selective synthesis of two octahedral ruthenium complexes.

A few years ago, several of us reported the isolation of eilatin **1a**, a marine alkaloid, from the tunicate *Eudistoma sp*.[1] This highly symmetric pyrido[2,3,4-*kl*]acridine was named after the location of its collection, the Gulf of Eilat. The bioactivity of eilatin[2] initiated a synthetic effort which yielded several syntheses,[3,4] the most efficient among them being biomimetic.[4] Herein we report a new aspect of eilatin character, namely its use as a face-selective ligand for transition metals.

The planar heptacyclic eilatin **1a** may be viewed as an all-conjugated 2,2′-bipyridine (bpy) and 2,2′-biquinoline (biq) fused rigidly back-to-back (**1b**). Both bpy and biq can serve as chelating ligands for various metals; however, their different steric bulk leads to different coordination behaviour. Thus, for instance, while both $[Ru(bpy)_3]^{2+}$ and $[Fe(bpy)_3]^{2+}$ are known compounds, the tris (biq) analogue is stable only for ruthenium,[5] while attempts to prepare the iron complex, $[Fe(biq)_3]^{2+}$, have been unsuccessful.[6] Accordingly, eilatin is expected to behave as a bidirectional ligand exhibiting face preference, depending on the steric crowding around the metal: in sterically demanding geometries such as octahedral or square-planar, eilatin is expected to bind to the metal through its 'head', while in loose geometries such as tetrahedral, both the 'head' and the 'tail' of eilatin are expected to be able to bind. Here, we describe the selective 'head' binding of eilatin to Ru^{II} in octahedral environment.

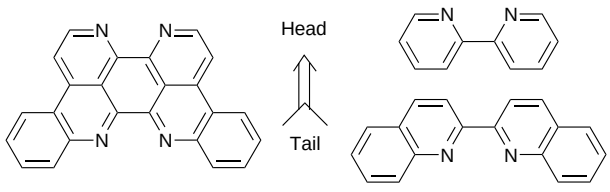
Octahedral complexes of the type $[RuL_nL'_{3-n}]^{2+}$ (L, L′ = bpy, phen, dppz,[7] HAT,[8] *etc*.) have attracted substantial scientific interest because of their remarkable MLCT properties,[9] directional electron and energy transfer,[10] DNA intercalation,[11,12] ability to serve as building blocks in supramolecular arrays,[13] and more. Reacting $[Ru(bpy)_2Cl_2]$ and eilatin in aqueous methanol and precipitating the product with ammonium hexafluorophosphate yielded $[Ru(bpy)_2(eilatin)][PF_6]_2$ **3a** as a dark green solid (Scheme 1).†

^{1}H NMR indicated the formation of a major product having C_2 symmetry in at least 90% selectivity, which was purified by crystallization.‡ Complete assignment of all the protons was possible using ^{1}H COSY, NOESY and HMQC two-dimensional NMR techniques. Two pieces of evidence supported the assignment of the major product as the expected 'head' isomer: (*i*) NOE connectivity between the H^a protons of eilatin and H^6 and $H^{6'}$ protons of the bipyridine units, indicating that the 'head' of eilatin is directed towards the metal, and (*ii*) ring-current effects on chemical shift: the H^a protons of eilatin are strongly shifted to a higher field relative to free eilatin in $(CD_3)_2SO$, while the other protons are only slightly affected, indicating close proximity of these 'head' protons to the orthogonal bipyridine rings. FABMS was consistent with the proposed mononuclear structure, indicating that the 'tail' side is not coordinated to a second metal atom.

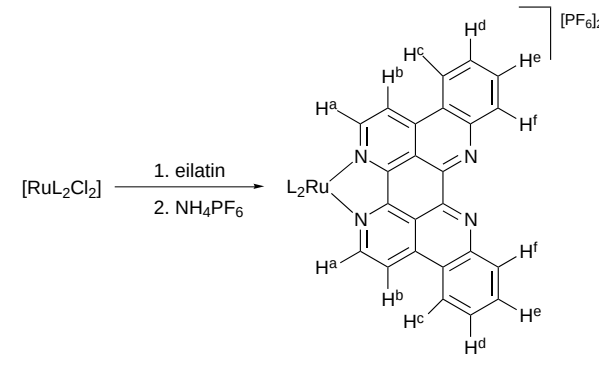
$[Ru(phen)_2Cl_2]$ reacted analogously yielding $[Ru(phen)_2(eilatin)][PF_6]_2$ **3b** as a dark green solid after work-up. The same high selectivity in formation of the major product was observed as for the bipyridine analogue. Using the same type of experiments and reasoning as for **3a** indicated that eilatin was bound 'head-on' in **3b** as well.‡

The ^{1}H NMR spectra of **3a** and **3b** exhibit a strong dependence of chemical shift on temperature; this effect is more pronounced when CD_3CN rather than $(CD_3)_2SO$ is used as solvent. Interestingly, different protons exhibit different temperature dependences: while the protons of the bpy or phen ligands in **3a** and **3b**, respectively, are almost unperturbed, the protons of the eilatin ligand (except for H^a) shift to lower field upon warming.§ Adding C_6D_6 to a CD_3CN solution of the complexes at a constant temperature has the same effect on the chemical shifts as raising the temperature. A possible explanation for this behaviour is the formation of intermolecular π stacks between eilatin ligands in **3a** or **3b**, which are broken as the temperature is raised, or when a competing solvent is added. A similar effect has been reported for $[Ru(bpy)_2(tpphz)]^{2+}$.[14]

The dark green colour of the two eilatin complexes stands in sharp contrast to the orange–red colour of $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ complexes. Table 1 lists the absorption maxima of free eilatin and its two ruthenium complexes. The two bands responsible for the green colour of **3a** and **3b** are the broad absorption centred at around 420 nm which is attributed to eilatin π–π* bands (perhaps overlapping Ru–bpy and Ru–phen MLCT bands in **3a** and **3b**, respectively), and the absorption at around 580 nm which is attributed to a Ru–eilatin MLCT band. This is one of the lowest energy MLCT bands reported for ruthenium polypyridyl complexes,[9] and is consistent with the



1a **1b**



2a L = bpy
b L = phen

3a L = bpy
b L = phen

Scheme 1

Table 1 Optical absorption data for eilatin and its ruthenium complexes

Compound	Absorption maxima[a]
1a[b]	242 (4.8), 286 (3.7), 360 (1.1), 388 (2.1), 408 (3.0), 434 (2.7)
3a[c]	241 (6.8), 286 (7.3), 341 (2.2), 405,[d] 424 (3.3), 460,[d] 583 (1.0)
3b[c]	224 (5.4), 263 (6.3), 292 (2.9), 341 (1.2), 405,[d] 423 (2.3), 460,[d] 581 (0.7)

[a] Absorption maxima are given in mm, and 10^{-4} ε (in parenthesis) in m^{-1} cm^{-1}. [b] From ref. 1 in methanol. [c] In acetonitrile. [d] Shoulder.

low lying π* orbital of eilatin.¶ This directional electron transfer could be important in the design of molecular devices.

In summary, we have shown that the potentially bifacial ligand, eilatin, prefers to bind through its less hindered face in a sterically demanding octahedral environment. We are currently investigating the electronic properties of the mononuclear complexes as well as the preparation of eilatin-bridged heteropolynuclear complexes.

Footnotes

† In a typical reaction 17 mg of $[Ru(bpy)_2Cl_2]\cdot 2H_2O$ and 1.5 equiv. of eilatin were heated to reflux in methanol–water for 5 h. Addition of water and evaporation of the methanol precipitated the excess eilatin, which was filtered off. Addition of NH_4PF_6 to the dark green aqueous solution precipitated **3a** as a PF_6 salt, which was purified by crystallization from an acetonitrile–ether mixture.

‡ *Spectroscopic data* for **1a**, **3a** and **3b**: **1a**, ^{1}H NMR [500 MHz, $(CD_3)_2SO$, 298 K]: δ 9.18 (H^a), 8.84 (H^b), 8.41 (H^c), 8.02 (H^d), 7.90 (H^e), 8.95 (H^f). **3a**, ^{1}H NMR [500 MHz, $(CD_3)_2SO$, 298 K]: δ 8.14 (H^a), 8.74 (H^b), 8.17 (H^c), 8.07 (H^d), 7.99 (H^e), 8.77 (H^f), 7.88 (H^6), 7.69 (H^5), 8.29 (H^4), 8.94 (H^3), 8.88 ($H^{3'}$), 8.17 ($H^{4'}$), 7.43 ($H^{5'}$), 7.98 ($H^{6'}$); FABMS, 771 $[M - 2PF_6 + H]^+$. **3b**, ^{1}H NMR [500 MHz, CD_3CN–$(CD_3)_2SO$, 302 K]: δ 8.07 (H^a), 8.51 (H^b), 8.18 (H^c), 7.98 (H^d), 7.91 (H^e), 8.68 (H^f), 8.07 (H^2), 7.75 (H^3), 8.74 (H^4), 8.34 (H^5,H6), 8.70 (H^7), 7.75 (H^8), 8.42 (H^9); FABMS, 819 $[M - 2PF_6 + H]^+$, 963 $[M - PF_6 + H]^+$.

§ Compare, for example, the effect of temperature on the ^{1}H NMR spectra of **3b** in CD_3CN. 298 K: δ 8.05 (H^a), 7.94 (H^b), 7.35 (H^c), 7.70 (H^d), 7.81 (H^e), 8.25 (H^f), 8.10 (H^2), 7.76 (H^3), 8.72 (H^4), 8.34 (H^5,H^6), 8.68 (H^7), 7.83 (H^8), 8.70 (H^9). 330 K: δ 8.07 (H^a), 8.23 (H^b), 7.89 (H^c), 7.89 (H^d), 7.89 (H^e), 8.48 (H^f), 8.12 (H^2), 7.76 (H^3), 8.70 (H^4), 8.33 (H^5,H^6), 8.67 (H^7), 7.80 (H^8), 8.55 (H^9).

¶ In contrast, the low-energy MLCT is absent from the spectra of pyridophenazine type complexes like $[Ru(bpy)_2(dppz)]^{2+}$[7] and $[Ru(bpy)_2(tpphz)]^{2+}$.[14]

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