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Dibenzoeilatin: a novel ligand exhibiting remarkable complementary π–π stacking interactions†

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The complex [Ru(bpy)$_2$(dbneil)][PF$_6$]$_2$ forms discrete dimers in solution held by strong π–π stacking interactions via its distorted dibenzoeilatin ligand, indicating that planarity is not an obligatory requirement for achieving strong π-stacking, as long as complementarity between the stacking moieties can be achieved.

π–π Stacking interactions between aromatic units are important non-covalent intermolecular forces that contribute to self-assembly and molecular recognition in a variety of supramolecular arrays.[1,2] There are several examples of systems that form supramolecular arrays in solution by self association *via* π–π stacking interactions alone.[3] However, only few systems address non-planar stacking moieties.[3a,g]

Recently, we have been studying supramolecular chemistry based solely on π–π stacking interactions. To this end, we explored the coordination chemistry of eilatin (**1**) (Fig. 1).[4] We have demonstrated that ruthenium(II) eilain complexes of the general formula [Ru(L–L)$_2$(eil)]$^{2+}$ (L–L = 2,2′-bipyridine, 1,10-phenanthroline, *etc.*; eil = eilatin) form discrete dimers held together by π–π stacking interactions in the solid state and in solution.[5] We were interested in expanding our studies to related ligands that would lead to complexes that exhibit modified and controlled π–π stacking interactions. In this paper we describe our initial results concerning the coordination chemistry of dibenzoeilatin (**2**), a highly symmetric eilatin analogue.

Dibenzoeilatin has a larger fused-aromatic area compared to eilatin that could lead to stronger π–π stacking interactions. On the other hand, dibenzoeilatin is expected to be distorted from planarity due to the steric hindrance between the H^d protons, based on similar known compounds (*e.g.* benzo[*c*]phenanthrene[6]). Revealing the relative effects of these seemingly opposing factors on the π–π stacking interactions of this ligand is intriguing.

The synthesis of this eilatin analogue was first reported by Kashman and coworkers in 1994,[7] but its solid state structure had not been reported. Following Kashman's methodology, we were able to obtain dibenzoeilatin on a convenient scale of 200 mg. Dibenzoeilatin turned out to be extremely insoluble, apparently due to the strong π–π stacking interactions, so crystallization was challenging. Eventually, we were able to grow single crystals suitable for X-ray diffraction from a mixture of chloroform, toluene, methanol and cyclohexane.‡ As expected, the dibenzoeilatin is distorted from planarity (Fig. 2) due to the overlapping hydrogens on adjacent benzo rings, thus retaining an 'S' conformation. In contrast, eilatin is planar.[8] The degree of distortion can be assessed from the root mean square (rms) deviation from planarity, which was found to be 0.173 Å. The existence of intermolecular π-stacking interactions between neighboring dibenzoeilatins could not be determined due to the large amount of disordered solvent molecules in the crystal lattice.

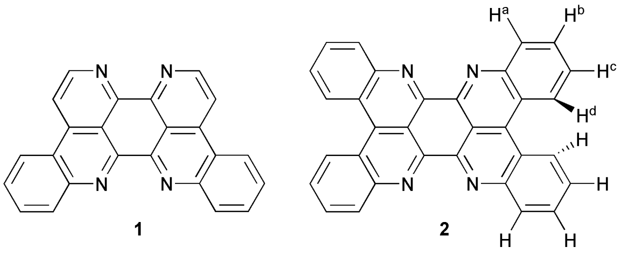

Fig. 1 Structure of eilatin (**1**) and dibenzoeilatin (**2**).

The head-to-tail directionality of eilatin does not apply for dibenzoeilatin, which is a homo bi-facial ligand. Therefore, it was uncertain whether a selective synthesis of a mononuclear Ru(II) complex of this ligand would be possible. Reacting *cis*-[Ru(bpy)$_2$Cl$_2$] with 1 equiv. of dibenzoeilatin in ethylene glycol at 140 °C for 8 h, followed by precipitation with aqueous KPF$_6$ yielded a dark green solid. The complex obtained was purified by several recrystallizations from CH$_3$CN/diethyl ether and was obtained in pure form in an overall yield of 57%.† At lower temperatures the reaction does not occur, in accordance with the greater steric hindrance that is present in dibenzoeilatin relative to eilatin. The ^{1}H NMR spectrum of the complex in CD$_3$CN indicated the selective formation of the mononuclear complex [Ru(bpy)$_2$(dbneil)][PF$_6$]$_2$ (**3**) (dbneil = dibenzoeilatin). This is evident from the eight different signals corresponding to dibenzoeilatin that is bound to the metal at only one of its two available coordination sites. In addition, eight different signals corresponding to the two bpy units are observed, in accordance with the expected C_2 symmetry of the complex on the NMR timescale. FAB-MS of the complex exhibited a [M − 2PF$_6$ + H] peak at m/z = 870.1, thus providing additional support for the formation of the mononuclear complex.

The ^{1}H NMR spectra of the complex change dramatically as a function of concentration. All the dibenzoeilatin protons (except for protons H^a and H^b, which face the metal center and are relatively shielded from intermolecular interactions such as π–π stacking) are markedly affected, exhibiting downfield shifts of up to 1.13 ppm upon dilution in the concentration range 0.1–1 mM. In contrast, the bpy protons shift upfield upon dilution and to a lower extent, *i.e.* up to 0.17 ppm.§ We attribute this concentration effect to π stacking of the complex in solution *via* its dibenzoeilatin moiety. Consistent with this hypothesis, increasing the temperature causes similar effects as dilution.

To attain further insight on the π–π stacking interactions of the complex, single crystals of **3** suitable for X-ray diffraction were obtained by recrystallization from CH$_3$CN/diethyl ether. The complex is of octahedral geometry (Fig. 3); however, the

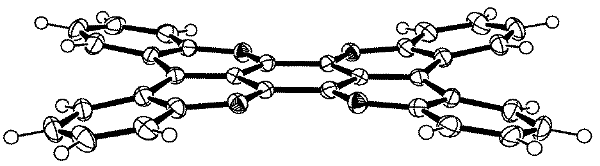

Fig. 2 Crystal structure of dibenzoeilatin (**2**). Disordered solvent molecules omitted for clarity.

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† Electronic supplementary information (ESI) available: experimental preparations and full identification of compounds. See http://www.rsc.org/suppdata/cc/b2/b206058b/

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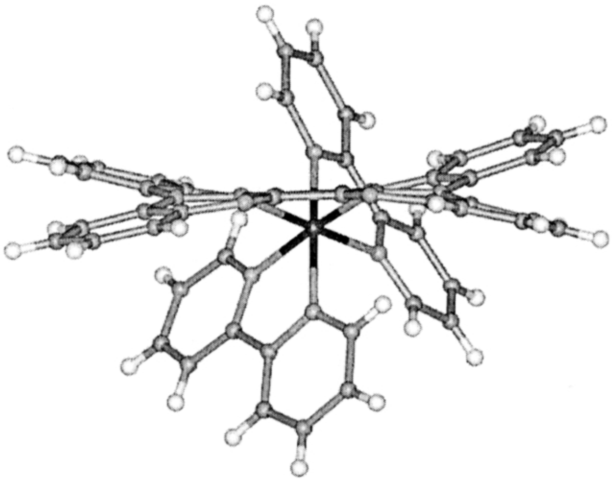

Fig. 3 Crystal structure of [Ru(bpy)$_2$(dbneil)][PF$_6$]$_2$ (**3**). Counter ions and solvent molecules omitted for clarity.

dibenzoeilatin ligand is ‘tilted’ with respect to the idealized equatorial plane of the RuN$_6$ octahedron. The ‘tilt’ conformation probably occurs as a result of steric interactions between the dibenzoeilatin and the bpy protons. The distances between the metal atom and the dibenzoeilatin nitrogens are 2.092 and 2.083 Å—only slightly longer than the typical value of *ca.* 2.06 Å.[9] In the ‘tilt’ conformation the dibenzoeilatin is rather shielded by the bpy ligands on one face and extremely exposed on the other face.

The unit cell (Fig. 4) consists of discrete dimers of **3** of opposite chirality, held together by π–π stacking interactions *via* the dibenzoeilatin moiety from its ‘exposed’ face. As a result, there hardly is any steric interference for the close approachment of the dibenzoeilatin ligands, and accordingly, the distance between the metal atoms in the dimer is 9.26 Å. In comparison, the Ru···Ru distance in the analogous [Ru(bpy)$_2$(eil)]$^{2+}$ complex is 11.05 Å, and the shortest distance found for eilatin complexes thus far is 10.26 Å.[5] The substantially shorter distance obtained for **3** represents a very close ‘interpenetration’ of the two aromatic planes. The dibenzoeilatin ligands π-stack in a *complementary* mode—so that their ‘S’ conformation is perfectly matched in the dimer.¶ The interplanar distance of the dibenzoeilatin ligands, *ca.* 3.6 Å, is typical of such π–π stacking.

As mentioned above, the ^{1}H NMR spectra exhibit only one set of signals, *i.e.* there is fast monomer–dimer equilibrium in solution. To attain a quantitative measurement of the π–π stacking interactions in solution, we used the method of Horman and Dreux[10] for calculating the dimerization constant K_D, that was found to be 750 ± 40 M^{-1} at 296.9 ± 0.1 K (for further details, refer to the ESI†). This value is *ca.* 2.5 times higher than that found for the analogous *rac*-[Ru(bpy)$_2$(eil)][PF$_6$]$_2$ complex.[5] All of the stated above indicate that despite the lack of planarity, the dibenzoeilatin moiety undergoes stronger π–π stacking interactions, probably due to the perfect complementarity in the dimer.

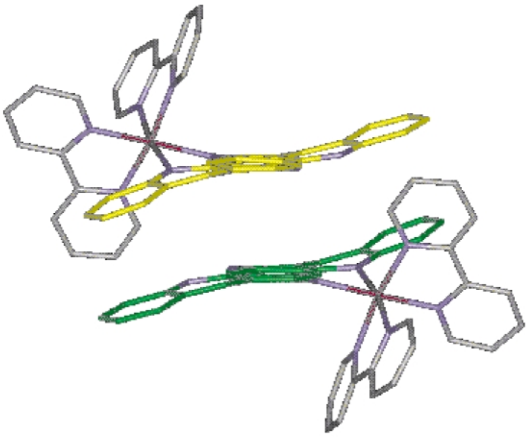

Fig. 4 Unit cell of [Ru(bpy)$_2$(dbneil)][PF$_6$]$_2$ (**3**), exhibiting π-stacking between dibenzoeilatin ligands. Counter ions and solvent molecules omitted for clarity.

In conclusion, we have shown that planarity is not an obligatory requirement for strong π–π stacking interactions, as long as complementarity between the stacking moieties can be achieved. We are currently exploring other parameters that may affect π-stacking interactions and their application in the construction of more complex supramolecular arrays based solely on π–π stacking interactions.

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Notes and references

‡ *Crystal data* for **2**: C$_{34}$H$_{18}$Cl$_6$N$_4$, M = 695.22, monoclinic, space group $P2_1/c$, a = 7.4600(2), b = 19.7320(5), c = 9.9440(2) Å, β = 101.5670(15)°, U = 1434.04(6) Å^3, D_c = 1.610 g cm^{-3} Z = 2, μ(Mo-Kα) = 0.634 mm^{-1}, T = 110(2) K, 3363 unique reflections were measured. The unit cell contains solvent molecules (chloroform), which could not be modeled precisely. R_1 = 0.0580 and wR_2 = 0.1294 for observations with $[I > 2\sigma(I)]$ and R_1 = 0.0942 and wR_2 = 0.1507 for all data.

Crystal data for **3**: C$_{60}$H$_{52}$F$_{12}$N$_8$O$_2$P$_2$Ru, M = 1308.11, triclinic, space group $P\bar{1}$, a = 13.2420(3), b = 14.3970(3), c = 17.4090(5) Å, α = 80.2500(17), β = 75.8620(12), γ = 64.2120(16)°, U = 2890.31(12) Å^3, D_c = 1.503 g cm^{-3}, Z = 2, μ(Mo-Kα) = 0.417 mm^{-1}, T = 110(2) K, 13111 unique reflections were measured. The structure contains partially disordered solvent (diethyl ether). The final refinement converged at R_1 = 0.0833 and wR_2 = 0.2107 for observations with $[I > 2\sigma(I)]$ and R_1 = 0.1460 and wR_2 = 0.2462 for all data.

CCDC 188874 and 188875. See http://www.rsc.org/suppdata/cc/b2/b206058b/ for crystallographic data in CIF or other electronic format.

§ The bpy proton H^6 shifts 0.45 ppm upfield upon dilution. This shift is attributed to proximity of this proton to the dibenzoeilatin nitrogen, as the N···H^6 distance is *ca.* 2.5 Å.

¶ The rms deviation of the dibenzoeilatin from planarity in **3** (0.274 Å) is even higher than in the free ligand and may result from the strong complementary π–π stacking interactions.

1 (*a*) C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2000, 3885–3896; (*b*) C. A. Hunter and J. K. M. Sanders, *J. Am. Chem. Soc.*, 1990, **112**, 5525–5534.

2 (*a*) For selected examples see: N. W. Alcock, P. R. Barker, J. M. Haider, M. J. Hannon, C. L. Painting, Z. Pikramenou, E. A. Plummer, K. Rissanen and P. Saarenketo, *J. Chem. Soc., Dalton Trans.*, 2000, 1447–1461; (*b*) H.-P. Wu, C. Janiak, G. Rheinwald and H. Lang, *J. Chem. Soc., Dalton Trans.*, 1999, 183–190; (*c*) C. Janiak, S. Deblon, H.-P. Wu, M. J. Kolm, P. Klüfers, H. Piotrowski and P. Mayer, *Eur. J. Inorg. Chem.*, 1999, 1507–1521; (*d*) D. Ranganathan, V. Haridas, R. Gilardi and I. L. Karle, *J. Am. Chem. Soc.*, 1998, **120**, 10793–10800.

3 (*a*) For selected examples see: A. S. Shetty, J. Zhang and J. S. Moore, *J. Am. Chem. Soc.*, 1996, **118**, 1019–1027; (*b*) E. Ishow, A. Gourdon and J.-P. Launay, *Chem. Commun.*, 1998, 1909–1910; (*c*) E. Ishow, A. Gourdon, J.-P. Launay, C. Chiorboli and F. Scandola, *Inorg. Chem.*, 1999, **38**, 1504–1510; (*d*) J. Bolger, A. Gourdon, E. Ishow and J.-P. Launay, *Inorg. Chem.*, 1996, **35**, 2937–2944; (*e*) A. Gourdon and J.-P. Launay, *Inorg. Chem.*, 1998, **37**, 5336–5341; (*f*) K. R. Koch, C. Sacht and C. Lawrence, *J. Chem. Soc., Dalton Trans.*, 1998, 689–695; (*g*) K. Nakamura, H. Okubo and M. Yamaguchi, *Org. Lett.*, 2001, **3**, 1097–1099.

4 A. Rudi, Y. Kashman, D. Gut, F. Lellouche and M. Kol, *Chem. Commun.*, 1997, 17–18.

5 D. Gut, A. Rudi, J. Kopilov, I. Goldberg and M. Kol, *J. Am. Chem. Soc.*, 2002, **124**, 5449–5456.

6 F. L. Hirshfeld, S. Snadler and G. M. J. Schmidt, *J. Chem. Soc.*, 1963, 2108.

7 G. Gellerman, A. Rudi and Y. Kashman, *Tetrahedron*, 1994, **50**, 12959.

8 The rms deviation from planarity for eilatin was calculated to be 0.044 Å. For crystal structure see: A. Rudi, Y. Benayahu, I. Goldberg and Y. Kashman, *Tetrahedron Lett.*, 1988, **29**, 6655–6656.

9 J. Breu and A. Stoll, *Acta Crystallogr., Sect. C*, 1996, **52**, 1174.

10 I. Horman and B. Dreux, *Helv. Chim. Acta*, 1984, **67**, 754–764.