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Towards dipyrrins: oxidation and metalation of acyclic and macrocyclic Schiff-base dipyrromethanes†

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Oxidation of acyclic Schiff-base dipyrromethanes cleanly results in dipyrrins, whereas the macrocyclic ‘Pacman’ analogues either decompose or form new dinuclear copper(II) complexes that are inert to ligand oxidation; the unhindered hydrogen substituent at the meso-carbon allows new structural motifs to form.

Bimetallic complexes with a well-defined molecular structure and controlled intermolecular separation are of significant interest in small molecule activation chemistry.1 In this context, several polypyrrolic Schiff-base macrocycles reported by us and others act as ligands for s-, d- and f-block metals.2–5 These complexes have a tendency to fold into cofacial or ‘Pacman’ structures that provide a reactive cleft between the two metals suited to cooperative catalytic reduction chemistry,6,7 with the macrocycles dissubstituted at each dipyrromethane meso-carbon position providing two dianionic coordination compartments.

A large number of dipyrrmethanes that are mono-substituted at the meso-position are readily oxidised to their dipyrrin congeners, most notably by 2,3-dichloro-5,6-dicyanobenzquinone (DDQ).8 Significantly, transition metal dipyrrin congeners, most notably by 2,3-dichloro-5,6-dicyanobenzquinone, are better suited to cooperative catalytic reduction chemistry,6,7 with the macrocycles dissubstituted at each dipyrrmethane meso-carbon position providing two dianionic coordination compartments.

The preparation of acyclic and macrocyclic dipyrrmethanes was achieved by exploiting the mono-meso-substituted dialdehyde 112 to form dimino-dipyrrmethane 2 in 74% yield using standard Schiff-base condensation methods (Scheme 1). The solid-state structure of 1 was determined by X-ray crystallography and is shown in the ESI.† The 1H NMR spectrum of 2 revealed the appearance of an imine proton resonance at 8.18 ppm accompanied by the loss of the aldehyde resonance of 1 at 9.24 ppm. The absorption band at 1623 cm−1 in the IR spectrum of 2 is assigned to the imine functional group.

Oxidation of 2 was achieved using stoichiometric amounts of DDQ to afford the dipyrrin HL1 in quantitative yield,13 and is supported by the loss of the meso-proton resonance at 5.69 ppm in the 1H NMR spectrum. Dipyrrin HL2 was synthesised by heating a toluene solution of 1 and 1BuNHz to 50 °C with Na2SO4, forming directly in air without a separate oxidation step. The 1H NMR spectrum of HL2 includes an imine proton resonance at 7.71 ppm and does not feature a meso-proton resonance. The IR absorption band at 1578 cm−1 is assigned to the imine functional group. The solid-state structure of HL2 was determined by X-ray crystallography (ESI†) and displays the expected planar meso-carbon geometry.

A C2-symmetric solution-state structure was observed for HL2 by NMR spectroscopy, but in the solid-state, one imine group is rotated away from the N4-pocket, lowering the symmetry to...
C1. HL2 crystallises as co-planar, π-stacked dimers, arranged head-to-tail.

Reaction between HL4 and LiN(SiMe3)2 cleanly generates the lithium dipyrrolyl LiL4 which was then used to form the iron(μ) complex FeBr(L1) by salt metathesis in THF. While not characterised by X-ray crystallography and NMR silent, ESI-MS of microcrystalline FeBr(L1) supports its formulation. The exclusion of air from these synthetic procedures avoids undesired ligand oxidation reactions which have been shown to occur on oxidation of Group 10 complexes of similar iminodipyromethane ligands.13

Electronic absorption spectra were recorded for 2, HL4 and the iron(μ) complex FeBr(L1) (Fig. 1), and the spectra for 2 and HL4 were accurately reproduced by TD-DFT calculations using the B3LYP functional and 6-311G(d,p) basis set (ESI†). The dominant absorption band for 2 appears at 373 nm and is assigned as a mixture of HOMO (H) to LUMO (L)+1 (59%) and (H−1)L (32%) transitions, with the H−L transition appearing as a shoulder at 413 nm. Upon oxidation to HL4, both the (H−1)L and H−L transitions are red-shifted to 520 and 540 nm, respectively, while the H−(L+1) transition remains in the UV-region at 290 nm. This change in electronic structure is typical for dipyrromethene compounds14 and reflects a 1.6 eV acid-promoted condensation of 1 with the appropriate diamine. Upon neutralisation with NEt3, the free-base precipitates cleanly from the methanol solution as a dull-yellow solid and is isolated by filtration. For both compounds, characteristic imine proton resonances were observed in the 1H NMR spectra at 8.09 ppm (H4L3) and 8.38 ppm (H4L4) and imine IR absorption bands at 1620 cm−1 (H4L3) and 1614 cm−1 (H4L4) were also recorded. No higher-order cyclisation products were observed by ESI-MS with only the expected molecular ions observed at 937 m/z for H4L3 and 1080 m/z for H4L4.

The solid-state structures for both H4L3 and H4L4 were determined by X-ray crystallography (Fig. 3). Surprisingly, and unlike previous examples, H4L3 crystallises excluding any protic solvent molecules that are usually hydrogen-bonded in the cleft.4,16 Instead, THF solvent molecules are hydrogen-bonded to each pyrrole group with each imino-pyrrole unit twisted with respect to its neighbouring units in a non-folded configuration that minimises ring-strain. Macrocycle H4L4 crystallises in a bowl geometry in which the anthracene groups are held further apart than they are common found in metal complexes; in this case, protic solvent molecules are present within the cleft.

The [2 + 2] cyclisation between 1 and the diamine could result in either syn- or anti-isomers in which the relative positions of the meso-substituents dictate the identity of the
isomer. Importantly, both H₄L³ and H₄L⁴ crystallise as the syn-isomer only and, furthermore, there is no evidence to support a mixture of isomers by NMR spectroscopy, which clearly shows a single set of resonances for ¹H, ¹³C and ¹⁹F nuclei. Considering the isolated yields of the macrocycles (ca. 40%), it is likely that some preferential precipitation of the syn-isomer has occurred, with the anti-isomer remaining in solution; we have, as yet, been unable to isolate or characterise material consistent with this latter isomer.

In contrast to the acyclic analogues, attempts to oxidise macrocycles H₄L³ and H₄L⁴ to the dipyrrins using DDQ resulted in decomposition to a myriad of unidentifiable products. Similar decomposition was observed on reaction of H₄L³ and H₄L⁴ with chloranil, Ag₂O, I₂ and Ce(NH₄)₂(NO₃)₆. Despite previous reports of dipyrrmethane macrocycles being successfully oxidised by MnO₂ or by KMnO₄, no discernible products have yet been isolated using these oxidants.

To investigate this further, the redox behaviour of HL², H₄L³ and H₄L⁴ was investigated by cyclic voltammetry. The CV for HL² includes a reversible reduction to the radical anion at E½ = −1.46 V vs. Fe⁺/Fe and a second, irreversible reduction at Epa = −2.28 V. This second process is assigned tentatively to the two-electron, proton-coupled reduction to the dipyrrmethane, H₄L³. The CVs for macrocycles H₄L³ and H₄L⁴ do not feature any oxidation processes, only an irreversible reduction at Epa = −1.41 V vs. Fe⁺/Fe for H₄L⁴ and Epa = −1.78 V for H₄L⁴ (ESI†).

As an alternative route to dipyrrins, attempts were made to oxidise H₄L³ and H₄L⁴ in air in the presence of a metal cation. As such, bimetallic copper(II) complexes were prepared by stirring THF solutions of H₄L⁴ with Cu(OAc)₂·H₂O in the presence of NEt₃ in air. The resulting cation. As such, bimetallic copper(II) complexes were prepared by stirring THF solutions of H₄L⁴ with Cu(OAc)₂·H₂O in the presence of NEt₃ in air. The resulting cation.

The solid-state structures for Cu₂(L³) and Cu₂(L⁴) were determined by X-ray crystallography (Fig. 4 and 5, and ESI† respectively) and in all cases show non-oxidised dipyrrmethane macrocycles, evident from the tetrahedral bond angles around each meso-carbon atom (mean a = 110.2° for Cu₂(L³) and 111.0° for Cu₂(L⁴)). This is in disagreement with the mass spectrometry data of these complexes and suggests that the macrocycles may oxidise under MS conditions.

Fig. 4 Solid state structure of Cu₂(L³)·4Py. For clarity, most H atoms and three pyridine solvent molecules are omitted (displacement ellipsoids drawn at 50% probability). Cu–Cu, 4.693(6) Å; sum of planar angles, 359.8° around Cu₁ and 359.0° around Cu₂; bite angle, 152°.

Unexpectedly, the o-phenylene-bridged macrocycle in Cu₂(L¹) adopts a ‘bowl’ conformation on metalation, bonding to the metal through two adjacent pyrrolic-imine groups and folding at the meso-carbon atoms, resulting in a wide bite angle of 152° between the two N₁ donor compartments and a torsional twist of 24.8(2)°; this results in a long Cu–Cu separation of 6.493(6) Å. These data contrast to those of copper(II) complexes of the meso-disubstituted macrocyclic analogues, which adopt ‘classical’ Pacman structures on metalation through hinging at the arene rings, and suggests that the macrocyclic topology is controlled through the choice (or absence) of meso-substituent; these latter Pacman complexes exhibit much smaller bite angles (52–62°) and shorter Cu–Cu separations of 3.47–4.05 Å. A structurally similar U(III) complex was recently reported to adopt a similar coordination geometry to Cu₂(L¹), but in bowl-shaped complexes of other metals, the pyrrole groups remain protonated and the two metal centres are bridged by anions, such as hydroxides.

Importantly, Cu₂(L³) crystallises as the syn-isomer only.

Due to the separation between the imine nitrogen donors in the anthracene-pillared macrocycle L⁵, a bowl configuration is not possible; as such, both Cu₂(L⁴) and Cu₂(L⁵) crystallise as Pacman complexes with 30° twist angles between the anthra-
cene groups and the diiminodipyrrromethane coordination pockets (Fig. 5). Again, the internuclear separation is controlled through choice of the meso-substituent, as Cu$_2$(L$^4$) has a significantly shorter Cu⋯Cu separation of 4.818(3) Å compared to 5.345(1) Å in Cu$_2$(L$^5$).

The internuclear distance in Cu$_2$(L$^4$) is also short compared to related complexes of Co(n), Pd(n) and U(vi) complexes of L$^5$ (5.377–5.834 Å)$^{18,21}$ and is more similar to that observed for dinuclear Zn(n) complexes of L$^5$ that are bridged by anions (3.871–5.532 Å).$^{22}$ The small meso-proton substituent also has the effect of closing the cleft, so that Cu$_2$(L$^4$) has a negative bite angle of −8.03° between the two N$_4$-donor planes, compared to the positive bite angle of 14.83° for Cu$_2$(L$^5$). As with Cu$_2$(L$^3$), Cu$_2$(L$^4$) crystallises as the syn, exo-isomer only, with no evidence for syn, endo- or anti-isomers.

The redox chemistry of Cu$_2$(L$^3$), Cu$_2$(L$^4$) and Cu$_2$(L$^5$) was investigated by cyclic voltammetry. The CVs of Cu$_2$(L$^3$) and Cu$_2$(L$^5$) showed no oxidation features, with only irreversible reductions for both at $E^o_p$ = −1.51 V vs. Fe$^2$/Fe for Cu$_2$(L$^3$) and $E^o_p$ = −1.70 V and $E^o_p$ = −2.30 V for Cu$_2$(L$^5$) (ESI†). In contrast, the CV of Cu$_2$(L$^4$) shows one quasi-reversible, two-electron oxidation at $E^o_p$ = −0.10 V and two quasi-reversible, one-electron reductions at $E^o_p$ = −1.47 V and $E^o_p$ = −1.76 V (Fig. 6). These redox events are assigned tentatively to the formation of Cu$_2$(L$^3$)−, Cu$_2$(L$^5$)−, and Cu$_2$(L$^4$)−, respectively, i.e. oxidation to Cu(n) and sequential reduction to Cu(0). The reversibility of these processes suggest they are metal-based; electrochemical oxidation of the macrocycle to the dipyrin is anticipated to be irreversible due to the loss of hydrogen atoms and the required change in geometry that would follow.

We have synthesised two new acyclic dipyrin compounds and two new Schiff-base macrocycles. These macrocycles are not readily oxidised to their dipyrin congeners, even when metalated, yet due to the sterically unhindered meso-carbon we have been able to prepare two new copper(n) macrocycle complexes that adopt unexpected structures with very dissimilar Cu⋯Cu separations; we are currently investigating the electronic structures and redox behaviours of these complexes by EPR spectroscopy and electrochemistry, as well as their reactivity towards CO$_2$ and other reducible substrates.

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**Notes and references**


