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

James R. Pankhurst, Thomas Cadenbach, Daniel Betz, Colin Finn and Jason B. Love*

Oxidation of acyclic Schiff-base dipyrrromethanes 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 internuclear 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 disubstituted at each dipyrrinmethane meso-carbon position providing two dianionic coordination compartments.

A large number of dipyrrromethanes that are mono-substituted at the meso-position are readily oxidised to their dipyrrin congeners, most notably by 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ).8 Significantly, transition metal dipyrrin congeners, most notably by 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ).8 Significantly, transition metal dipyrrin 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 disubstituted at each dipyrrinmethane meso-carbon position providing two dianionic coordination pockets to stabilise metals in lower oxidation states and hence favour small molecule reduction chemistry.

The preparation of acyclic and macrocyclic dipyrrromethanes was achieved by exploiting the mono-meso-substituted dialdehyde 112 to form diminodipyrromethane 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 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 BuNH2 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-carbon resonance. The IR absorption band at 1582 cm−1 is assigned to the imine functional group.

EaStCHEM School of Chemistry, University of Edinburgh, Joseph Black Building, David Brewster Road, Edinburgh, EH9 3FJ, UK. E-mail: jason.love@ed.ac.uk

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Scheme 1 Syntheses of acyclic and macrocyclic dipyrrinmethane (2, H2L3, H4L4) and dipyrrin compounds (HL1, HL2).
typical for dipyrromethene compounds and reflects a 1.6 eV absorption band for H
oxygen N4 is rotated out of the pocket and is not co-ordinated. As with H
L1(μ-O)FeX core (X = halide) are seen in the UV-region at 290 nm. This change in electronic structure is typical for dipyrromethene compounds and reflects a 1.6 eV absorption band for H
oxidation of Group 10 complexes of similar iminodipyrrin {FeBr(L)}, H(L) and H(L+1) transitions are red-shifted to 520 and 540 nm, respectively, while the H–L transition appearing as a shoulder at 413 nm. Upon oxidation to FeBr(L), both the (H–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 compounds and reflects a 1.6 eV stabilisation of the LUMO upon oxidation. Although the extinction coefficients of 20 000 M−1 cm−1 for H(L) and FeBr(L) are small compared to BODIPY compounds (80 000 M−1 cm−1) they are similar to pyrromethane-BF3 complexes.
A small number of crystals were grown from THF–hexane solutions of FeBr(L), and were found to be the oxidised iron(III) oxo dipyrrin {FeBr(L)}2(μ-O) (Fig. 2) in which the Fe centres are five-coordinate and adopt a distorted trigonal bipyramidal geometry with pyrrole N1, Br1, and O1 equatorial and pyrrole N3 and imine N2 axial. As with H(L), one imine nitrogen N4 is rotated out of the pocket and is not co-ordinated. The overall dinuclear structure is reminiscent of a Pacman arrangement, with perfluoroaryl groups and 3-Bu-aryl substituents adjacent. The XFe(μ-O)FeX core (X = halide) is common in Fe chemistry, albeit usually as part of a wholly inorganic anion.
The ortho-phenylene bridged macrocycle H4L3 and the 1,8-anthracene bridged macrocycle H4L4 were both prepared by 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 prootic solvent molecules that are usually hydrogen-bonded in the cleft. 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 commonly found in metal complexes; in this case, prootic 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
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isomer. Importantly, both H₄L³ and H₂L⁴ 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 H₂L⁴ to the dipyrrins using DDQ resulted in decomposition to a myriad of unidentifiable products. Similar decomposition was observed on reaction of H₄L³ and H₂L⁴ with chloranil, Ag₂O, I₂ and Ce(NH₄)₂(NO₃)₆. Despite previous reports of dipyrrin 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 HL³, H₄L³ and H₂L⁴ was investigated by cyclic voltammetry. The CV for HL² includes a reversible reduction to the radical anion at E₁/₂ = −1.46 V vs. Fe⁺/Fe and a second, irreversible reduction at Eₚ = −2.28 V. This second process is assigned tentatively to the two-electron, proton-coupled reduction to the dipyrrinmethane, H₄L³. The CVs for macrocycles H₄L³ and H₂L⁴ do not feature any oxidation processes, only an irreversible reduction at Eₚ = −1.41 V vs. Fe⁺/Fe for H₂L⁴ and Eₚ = −1.78 V for H₄L⁴ (ESI†).

As an alternative route to dipyrrins, attempts were made to oxidise H₄L³ and H₂L⁴ in air in the presence of a metal cation. As such, bimetallic copper(n) complexes were prepared by stirring THF solutions of H₄L³ or H₂L⁴ with Cu(OAc)₂·H₂O in the presence of NEt₃ in air. The resulting dipyrrinmethane complexes Cu₂(L³) and Cu₂(L⁴) were found to be stable on alumina and were thus purified by column chromatography, eluting the pure products as orange CH₂Cl₂ fractions in high yields; ‘accordion’ macrocycles that have dipyrrinmethane head groups but flexible compartmental spacers display similar inertness to oxidation on metalation. The synthesises of these compounds are supported by ESI-MS, with molecular ion peaks at 1058 m/z for Cu₂(L³) and 1203 m/z for Cu₂(L⁴) with the expected isotope pattern for bimetallic complexes, albeit with seemingly oxidised macrocycles. The vibrational frequencies for the imine groups at 1552 cm⁻¹ for Cu₂(L³) and 1574 cm⁻¹ for Cu₂(L⁴) are lower compared to the free ligands and are indicative of metalation. Both compounds are NMR-silent. The copper(n) complex Cu₂(L³) that is similar to Cu₂(L⁴), but differs in that the macrocycle is diethyl-substituted at the meso-position, was also made for comparison (ESI†).

The solid-state structures for Cu₂(L³), Cu₂(L⁴), and Cu₂(L⁵) were determined by X-ray crystallography (Fig. 4 and 5, and ESI† respectively) and in all cases show non-oxidised dipyrrinmethane 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.

Unexpectedly, the o-phenylene-bridged macrocycle in Cu₂(L⁵) adopts a ‘bowl’ conformation on metalation, bonding to the metal through two adjacent pyrrolide-imine groups and folding at the meso-carbon atoms, resulting in a wide bite angle of 152° between the two N₄-donor components 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(n) complexes of the meso-dissubstituted 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(m) complex was recently reported to adopt a similar coordination geometry to Cu₂(L⁵) 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(L⁵) 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(L³) 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$^3$).

The internuclear distance in Cu$_2$(L$^4$) is also short compared to related complexes of Co(ii), Pd(ii) and U(vi) complexes of L$^5$ (5.377–5.834 Å)$^{7,21}$ and is more similar to that observed for dinuclear Zn(ii) complexes of L$^3$ that are bridged by anions (3.871–5.532 Å). The small meso-proton substituent also has the effect of closing the cleft, so that Cu$_2$(L$^3$) has a negative bite angle of –8.03° between the two N$_2$-donor planes, compared to the positive bite angle of 14.83° for Cu$_2$(L$^3$). 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$^4$) and Cu$_2$(L$^5$) showed no oxidation features, with only irreversible reductions for both at $E^0_p$ = –1.51 V vs. Fe$^{3+}$/Fe for Cu$_2$(L$^4$) and $E^0_p$ = –1.70 V and –2.30 V for Cu$_2$(L$^5$) (ESIS). In contrast, the CV of Cu$_2$(L$^3$) shows one quasi-reversible, two-electron oxidation at $E^0_p$ = –0.10 V and two quasi-reversible, one-electron reductions at $E^0_p$ = –1.47 V and –1.76 V (Fig. 6). These redox events are assigned tentatively to the formation of Cu$_2$(L$^3$)$^{2+}$, Cu$_2$(L$^3$)$^+$, and Cu$_2$(L$^3$)$^{−}$, respectively, i.e. oxidation to Cu[m] and sequential reduction to Cu(i). The reversibility of these processes suggest they are metal-based; electrochemical oxidation of the macrocycle to the dipyrrin 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 dipyrrin compounds and two new Schiff-base macrocycles. These macrocycles are not readily oxidised to their dipyrrin congeners, even when metalated, yet due to the sterically unhindered meso-carbon we have been able to prepare two new copper(ii) macrocyclic 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**


