Preparation and characterization of asymmetric α-alkoxy dipyrrin ligands and their metal complexes†

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Asymmetric α-substituted dipyrrins have been synthesized and characterized. The compounds were formed by a metal mediated reaction involving a single alkoxy group substituted into the α-position of an α,β-unsubstituted dipyrrin. An α-methoxy dipyrrin, 5-(4-cyanophenyl)-1-methoxydipyrrin (α-OMe-4-cydpm), was prepared from 5-(4-cyanophenyl)-4,6-dipyrromethane. Methoxy, ethoxy, and propoxy derivatives (α-OMe-4-mecdpm, α-OEt-4-mecdpm, α-OPr-4-mecdpm) of 5-(4-methoxycarbonylphenyl)-4,6-dipyrromethane have also been prepared. A homoleptic, bis(1-methoxy)-dipyrrinato zinc(II) complex, [Zn(α-OMe-4-mecdpm)$_2$], has been synthesized, as has a heteroleptic cobalt(III) complex with one α-OMe-4-cydpm ligand and two unsubstituted 5-(4-cyanophenyl)dipyrrin (4-cydpm) ligands ([Co(α-OMe-4-cydpm)(4-cydpm)$_2$]). The rotational barrier of the *meso*-aryl substituent of [Zn(α-OMe-4-mecdpm)$_2$] was found to be 17.3 kcal mol^{-1} by variable-temperature NMR spectroscopy. The compounds α-OMe-4-cydpm and [Zn(α-OMe-4-mecdpm)$_2$] have also been characterized by X-ray diffraction. The formation of the new dipyrrin derivatives is shown to be general and can be performed on dipyrrins with various *meso*-aryl substitutents, with a variety of alcohols, and can be promoted by several metal salts.

Introduction

Dipyrrins are an important class of conjugated, bipyrrolic chelators that have received increasing attention in recent years. Asymmetrically substituted dipyrromethanes and dipyrrins have been used extensively in the synthesis of porphyrins,[1–3] boron dipyrrin (BODIPY) dyes,[4,5] and supramolecular dimers and trimers.[6–9] *meso*-Substituted dipyrrins form a variety of discrete supramolecular structures,[10–13] coordination polymers,[11,12,14,15] and metal–organic frameworks.[16,17] Asymmetrically α-substituted, *meso*-aryl dipyrrin compounds (Fig. 1), and their corresponding metal complexes, have been prepared as precursors to porphyrins, and porphyrin derivatives, or have been isolated as side products during porphyrin syntheses.[18–22] Substitution by alkoxy groups at the α-position of N-confused porphyrins has also been reported.[23–30] The α-positions of dipyrrins and N-confused porphyrins are known to be rather reactive, undergoing transformations such as bromine-substitution,[31] Diels–Alder reactions,[32] and ring fusion.[31,33] Polypyrrolic compounds with oxygen atoms in the α-position have been identified in several natural products and natural product derivatives[34] including, phycobilins,[35] phytochromes,[36] and bile pigments.[37,38]

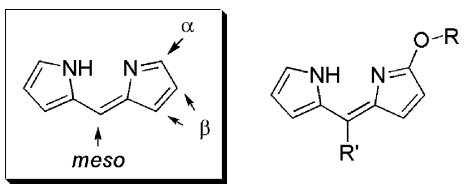

Fig. 1 The α-, β-, and *meso*-positions in dipyrrins (left). Generic structure of the asymmetric α-alkoxy *meso*-substituted dipyrrin described in this report (right).

Herein, a route to asymmetric α-substituted *meso*-dipyrrins has been discovered and investigated. The compounds are formed by the substitution of an alkoxy group into the α-position of a dipyrromethane during oxidation to the corresponding dipyrrin (Fig. 1). These compounds were initially detected as side products from the synthesis of various metal dipyrrinato complexes. Further tests revealed more favorable conditions to obtain the alkoxy substituted dipyrrin, without the formation of metal complexes. A series of these asymmetric α-alkoxy dipyrrins, as well as metal complexes of this ligand with cobalt(III) and zinc(II), have been prepared and characterized. The synthetic route to asymmetric α-alkoxy dipyrrins described here may prove useful, upon further optimization, for the synthesis of interesting new ligands, chromophores, or natural products containing this functional motif.

Results and discussion

In ongoing synthetic efforts in our laboratory, *meso*-substituted dipyrromethanes were being prepared using standard methods,[39–42] followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) or *p*-chloranil to form the corresponding dipyrrins *in situ* (Scheme 1) for use in the synthesis of dipyrrinato coordination complexes.[14,16,43] During some of these preparations, we observed the formation of a new compound *via* TLC (as a mobile yellow band), an apparent side product during metal complex formation.

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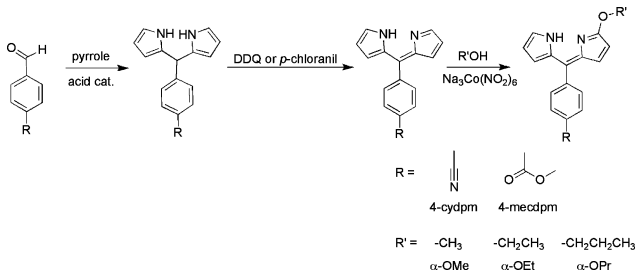
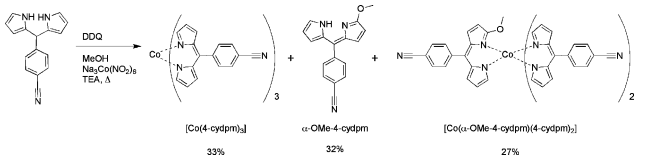
† Electronic supplementary information (ESI) available: Crystallographic details, Fig. S1–S15 (includes NMR spectral data of all new compounds). See DOI: 10.1039/b615801c



Scheme 1 Synthesis of dipyrromethanes, dipyrromethenes, and α-alkoxy dipyrromethenes.



Scheme 2 Synthesis of α-OMe-4-cydpm, [Co(4-cydpm)$_3$], and [Co(α-OMe-4-cydpm)(4-cydpm)$_2$] from 5-(4-cyanocarbonylphenyl)-4,6-dipyrromethane.

Our initial observation specifically involved a reaction with 5-(4-cyanophenyl)-4,6-dipyrromethene (4-cydpm), $Na_3Co(NO_2)_6$, and triethylamine in a 1 : 5 mixture of methanol and chloroform (Scheme 2). This reaction was designed to form the complex [Co(4-cydpm)$_3$], but yielded three products each in modest yields (~25–35% each). The components of this mixture were separated by silica column chromatography for identification. The first product to elute from the column was isolated as a red solid and was identified as the expected [Co(4-cydpm)$_3$] complex.[17] The second product to elute was isolated as a yellow solid and after extensive characterization determined to be an α-methoxy dipyrrin (α-OMe-4-cydpm). The last product to elute from the column was found to be a dark red solid, suggestive of a cobalt(III) dipyrrinato complex. NMR spectroscopy and mass spectrometry indicated that this was indeed a cobalt(III) complex, containing an unusual ligand set of two unaltered dipyrrinato and one α-methoxy dipyrrinato ligand ([Co(α-OMe-4-cydpm)(4-cydpm)$_2$]).

Exploring the reaction conditions

Various reaction conditions were used to examine the formation and isolation of the new asymmetric dipyrrin compounds. It was found that the formation of the alkoxy-substituted compounds did not require the presence of a base but did require a metal salt. The use of bases such as triethylamine promoted the formation of the dipyrrinato metal complexes over the formation of the new alkoxy-substituted dipyrrins. In the absence of base formation of the dipyrrinato metal complex was minimized with no change in the yield of the alkoxy substituted species. Reducing the quantity of metal salts to catalytic amounts (5 mol% of $Na_3Co(NO_2)_6$ *versus* the dipyrromethane) resulted in very slow reactions, which required several days at room temperature. Therefore, 0.3–0.4 equivalents of the metal source was used, as employed in our initial discovery, and the reaction was heated to reflux. These reaction conditions constituted a general approach to asymmetric α-alkoxy dipyrrins, consisting of the oxidation of a dipyrromethane followed by *in situ* reaction of the resulting dipyrrin with a metal salt in the presence of an alcohol. While these conditions did not improve the yield of the asymmetric α-alkoxy dipyrrin *per se* (based on our original observations), it did reduce the number of products detected as mobile bands by TLC. This method greatly facilitated purification, as the asymmetric α-alkoxy dipyrrin was the only major product formed that was readily eluted from silica gel column chromatography.

Further experiments were also performed to probe the reaction conditions and to attempt to improve the yield. These efforts explored alternative solvents, alcohols, oxidants, metal salts, and dipyrrin precursors. The results are summarized in Table 1.

Table 1 Reaction conditions evaluated for the formation of α-alkoxy dipyrrins. Reactions deemed successful but not fully characterized were evaluated by TLC and electronic absorption spectroscopy[a]

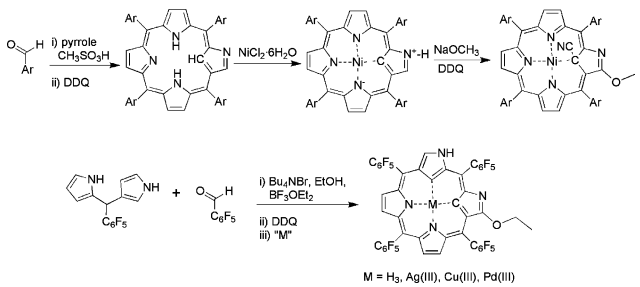
Dipyrromethane	Oxidant	Solvent	Alcohol	Metal salt	Isolated yield or conversion
(4-mecdp)methane	DDQ	$CHCl_3$	MeOH	$Na_3Co(NO_2)_6$	19% yield
(4-mecdp)methane	*p*-Chloranil	$CHCl_3$	MeOH	$Na_3Co(NO_2)_6$	35% yield
(4-cydp)methane	DDQ	$CHCl_3$	MeOH	$Na_3Co(NO_2)_6$	15% yield
(4-dp)methane	DDQ	$CHCl_3$	MeOH	$Na_3Co(NO_2)_6$	Product detected by TLC
(4-mtdp)methane	DDQ	$CHCl_3$	MeOH	$Na_3Co(NO_2)_6$	Product detected by TLC
(4-ntdp)methane	DDQ	$CHCl_3$	MeOH	$Na_3Co(NO_2)_6$	No product detected
(4-mecdp)methane	DDQ	CH_2Cl_2	MeOH	$Na_3Co(NO_2)_6$	Product detected by TLC
(4-mecdp)methane	DDQ	THF	MeOH	$Na_3Co(NO_2)_6$	Product detected by TLC
(4-mecdp)methane	DDQ	Benzene	MeOH	$Na_3Co(NO_2)_6$	Product detected by TLC
(4-mecdp)methane	DDQ	EtOAc	MeOH	$Na_3Co(NO_2)_6$	No product detected
(4-mecdp)methane	DDQ	CH_3CN	MeOH	$Na_3Co(NO_2)_6$	No product detected
(4-mecdp)methane	DDQ	$CHCl_3$	EtOH	$Na_3Co(NO_2)_6$	35% yield
(4-mecdp)methane	DDQ	$CHCl_3$	PrOH	$Na_3Co(NO_2)_6$	38% yield
(4-mecdp)methane	DDQ	$CHCl_3$	iPrOH	$Na_3Co(NO_2)_6$	Product detected by TLC
(4-mecdp)methane	DDQ	$CHCl_3$	BnOH	$Na_3Co(NO_2)_6$	Product detected by TLC
(4-mecdp)methane	DDQ	$CHCl_3$	MeOH	$Mn(OAc)_2{\cdot}4H_2O$	13% yield
(4-mecdp)methane	DDQ	$CHCl_3$	MeOH	$FeCl_3{\cdot}6H_2O$	15% yield
(4-mecdp)methane	DDQ	$CHCl_3$	MeOH	$[Co(pyr)_4Cl_2]Cl$	Product detected by TLC
(4-mecdp)methane	DDQ	$CHCl_3$	MeOH	$Cu(acac)_2$	No product detected

[a] Select abbreviations: DDQ, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone; (4-mecdp)methane, 5-(4-methoxycarbonylphenyl)-4,6-dipyrromethane; (4-cydp)methane, 5-(4-cyanophenyl)-4,6-dipyrromethane; (4-dp)methane, 5-(4-phenyl)-4,6-dipyrromethane; (4-mtdp)methane, 5-(4-methylthiophenyl)-4,6-dipyrromethane; (4-ntdp)methane, 5-(4-nitrophenyl)-4,6-dipyrromethane.

Non- or weakly-coordinating solvents such as CH_2Cl_2, THF, and benzene were tolerated, while more polar, coordinating solvents such as ethyl acetate and CH_3CN inhibited formation of the desired product, leaving the unsubstituted dipyrrin. The use of alcohol substrates other than methanol, such as ethanol, propanol, isopropanol, and benzyl alcohol, was successful; however, the yield from the substitution of isopropanol and benzyl alcohol was extremely low. No attempts to further optimize the reaction conditions for these substrates were explored. Several metal salts were tested with methanol and found to be competent to perform the desired reaction (albeit in lower isolated yields), including $Mn(OAc)_2{\cdot}4H_2O$, $FeCl_3{\cdot}6H_2O$, and $[Co(pyr)_4Cl_2]Cl$. In contrast, $Cu(acac)_2$ failed to promote the reaction, which was expected as dipyrrinato ligands rapidly form copper(II) complexes in the absence of base.[14,43] From these experiments it appears that the reaction scope is limited to metal ions, such as manganese(II), iron(III), and cobalt(III), that do not readily form dipyrrinato complexes under the reaction conditions. While an extensive study of the different reaction conditions has been performed without an improvement in the yield, a more comprehensive investigation may also reveal higher yielding preparations.

Testing of additional reaction conditions revealed another essential component involved in the formation of the alkoxy dipyrrins. Several important observations were made: (1) When purified 4-mecdpm was reacted with $Na_3Co(NO_2)_6$ in a methanol solution, the α-substitution did not occur. (2) The alkoxy substitution also did not occur upon addition of DDQ to a solution of purified 4-mecdpm. (3) When 2,3,5,6-tetrachlorohydroquinone (the reduced form of *p*-chloranil) was added to a reaction mixture of pure 4-mecdpm, $Na_3Co(NO_2)_6$, and methanol, α-OMe-4-mecdpm was formed. Thus, it appears that the hydroquinone is required for the alkoxy-substitution to occur. It should be noted that 2,3-dichloro-5,6-dicyanohydroquinone would have been present under the original reaction conditions as the product of the reduction of DDQ.

The contribution of the hydroquinone in the formation of the α-substituted dipyrrins is consistent with a mechanism proposed by Dolphin and coworkers involving alkoxy substitution of an N-confused porphyrin (Scheme 3).[23] The reported reaction involves the addition of $NaOCH_3$ and DDQ to an N-confused porphyrin in a mixture of CH_2Cl_2/MeOH. The methoxy α-substituted porphyrin was only obtained in 9% yield. As reported in reference 23, we were able to isolate the re-oxidized hydroquinone (*p*-chloranil) from the reaction mixture. In the same report it was also proposed that the cyano group of the 2,3-dichloro-5,6-dicyanohydroquinone was involved. However, in our system, use of 2,3,5,6-tetrachlorohydroquinone, which does not contain a cyano moiety, gave the desired products. Osuka, Furuta *et al*. have also isolated various N-confused porphyrins that have a methoxy or ethoxy group substituted in the α-position of the confused pyrrole ring (Fig. 3).[24–30] These reactions utilize NaOMe or BF_3OEt and have been reported both with and without the presence of 2,3-dichloro-5,6-dicyano-hydroquinone. Overall, the essential components of the present reaction have been elucidated, but the mechanism of the reaction reported here will require further investigation.



Scheme 3 Reported reaction schemes for N-confused porphyrins by Dolphin (top) and Osuka (bottom) that contain alkoxy group substitution at the α-positions.

Spectroscopic and structural features of α-alkoxy dipyrrins

Several of the α-alkoxy dipyrrin compounds have been examined by mass spectrometry, electronic, infrared, and NMR spectroscopy. The electronic spectroscopy of the α-alkoxy dipyrrin moiety has an absorbance maximum at 407 nm ($\varepsilon \sim 20000\ M^{-1}\ cm^{-1}$, attributed to the π–π* transition, Fig. S15†), slightly shifted to higher energy when compared to that of the corresponding unsubstituted dipyrrins (~435 nm).[43] The NMR spectra of the α-alkoxy dipyrrins also have features distinct from the parent dipyrrins. For example, the ^1H NMR spectrum of α-OMe-4-cydpm shows five unique resonances (Fig. S5†), one for each of the pyrrolic protons (compared with three resonances for the symmetric dipyrrin). The hydrogen bound to the pyrrolic nitrogen atom, which is generally not observed in the NMR spectra of the dipyrrin precursors,[43] is readily located at 12.1 ppm for α-OMe-4-cydpm.

In addition to complete spectroscopic characterization, the compound α-OMe-4-cydpm was crystallized and the structure was determined by single-crystal X-ray diffraction (Table 2). The crystal structure reveals several interesting structural features, which again distinguish the compound from the parent unsubstituted dipyrrin (Fig. 2). First, the structure unambiguously reveals the constitution of the molecules, showing the methoxy substituent in the α-position of one of the pyrrolic subunits of the dipyrrin. Second, unlike the fully delocalized, aromatic structure of unsubstituted dipyrrins the crystal structure of α-OMe-4-cydpm reveals a distinct asymmetry in the bond lengths of the bipyrrolic chromophore. The structure reveals alternating short and long C–C and C–N bond distances in the α-substituted pyrrolic ring: 1.30 Å (N1–C1), 1.45 Å (C1–C2), 1.35 Å (C2–C3), and 1.46 Å (C3–C4).

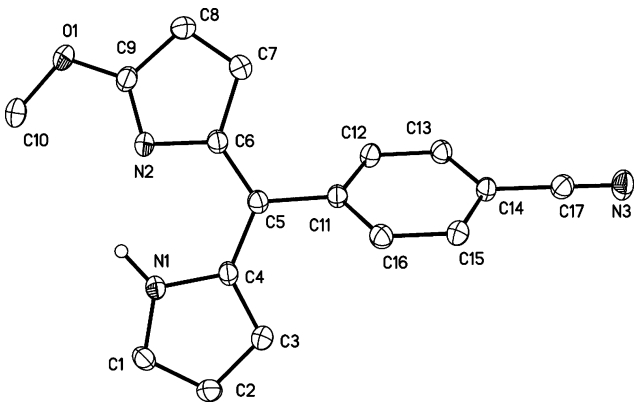


Fig. 2 Structural diagram of α-OMe-4-cydpm with partial atom numbering scheme (50% probability ellipsoids). Hydrogen atoms (except for the pyrrolic hydrogen) have been omitted for clarity.

However, this does not disrupt the delocalized nature of the unsubstituted pyrrole ring, which has bond distances of N2–C9 (1.36 Å), C9–C8 (1.38 Å), C8–C7 (1.41 Å), and C7–C6 (1.39 Å). The bond lengths agree well with an earlier crystal structure of a highly functionalized asymmetric α-methoxy dipyrrin.[44] Finally, the nitrogen-bound pyrrolic hydrogen atom (H1N), expected to be bound equally by either pyrrole ring in a dipyrrin, was identified in the electron density difference map of α-OMe-4-cydpm localized on the nitrogen atom of the unmodified pyrrole ring (Fig. 2). This may explain why this proton was readily observed by ^{1}H NMR, and suggests that the alkoxy group decreases the basicity of the nitrogen of the α-substituted pyrrole, favoring a single tautomeric form.

Metal α-alkoxy dipyrrin complexes

The α-alkoxy dipyrrins demonstrated the capacity to bind metal ions, as demonstrated by the cobalt(III) reaction mixture from which the compound was first identified (*vide supra*). A complex containing a single α-OMe-4-cydpm and two 4-cydpm ligands ([Co(α-OMe-4-cydpm)(4-cydpm)$_2$]) was isolated from the mixture of products. The cobalt(III) complex was characterized by high-resolution mass spectrometry, ^{1}H NMR, electronic, and IR spectroscopy. The α-methoxy substituent was found to significantly perturb the ligand-to-metal charge transfer (LMCT) band (400–620 nm) relative to the unsubstituted dipyrrinato complexes. As shown in Fig. 3, the electronic absorbance spectra of the unsubstituted and α-methoxy-substituted dipyrrinato cobalt(III) complexes are easily distinguishable. The unsubstituted complex [Co(4-cydpm)$_3$] has absorbance maxima at 469 and 506 nm, while the methoxy-substituted [Co(α-OMe-4-cydpm)(4-cydpm)$_2$] has a broad absorbance with a maximum at 490 nm. Although the complex [Co(α-OMe-4-cydpm)(4-cydpm)$_2$] contains only a single modified ligand, it is still readily detected and distinguished by the absorption spectrum.

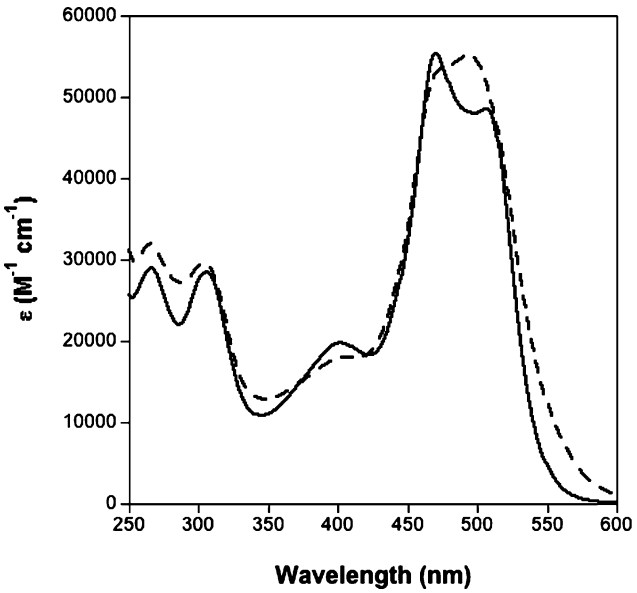


Fig. 3 Electronic absorption spectra for [Co(4-cydpm)$_3$] (—) and [Co(α-OMe-4-cydpm)(4-cydpm)$_2$] (---) in CH_2Cl_2.

The asymmetry afforded by the presence of the α-OMe-4-cydpm ligand in [Co(α-OMe-4-cydpm)(4-cydpm)$_2$] has a pronounced effect on the ^{1}H NMR spectrum of the complex (Fig. S4†). The protons associated with the dipyrrin core moieties of the complex exhibit unique chemical shifts, as can be seen by the numerous resonances from 6.0–7.0 ppm. These resonances appear as a combination of singlets, associated with the α-protons, and doublets associated with the β-protons. The phenyl protons of all three ligands also exhibit unique chemical shifts as can be seen by the multiplets at 7.4–7.8 ppm. The dipyrrinato, phenyl, and methoxy protons integrate to 18, 12, and 3 protons, respectively, indicating that the compound contains only one methoxy substituted dipyrrin ligand per metal complex. Efforts to recrystallize [Co(α-OMe-4-cydpm)(4-cydpm)$_2$] did not generate single crystals suitable for X-ray diffraction. Also, attempts to prepare homoleptic tris-chelate cobalt(III) complexes with three α-OMe-4-cydpm (or α-OMe-4-mecdpm) ligands were unsuccessful.

In an attempt to prepare a homoleptic metal complex with an α-alkoxy dipyrrinato ligand, we anticipated that a 4-coordinate, tetrahedral metal ion such as copper(II) or zinc(II) would better accommodate the sterics of the α-alkoxy dipyrrinato ligand. Indeed, zinc(II) complexes previously have been prepared from asymmetric dipyrrins.[20,22] The combination of α-OMe-4-mecdpm, $Zn(OAc)_2{\cdot}2H_2O$, and triethylamine in a chloroform/methanol mixture at room temperature generated the desired complex, which was crystallized upon slow evaporation from the reaction mixture. Unlike other zinc(II) dipyrrinato complexes studied in our laboratory, [Zn(α-OMe-4-mecdpm)$_2$] was not stable to purification by column chromatography,[45,46] as exposure of [Zn(α-OMe-4-mecdpm)$_2$] to silica caused decomposition of the complex, regenerating the free ligand. Electronic absorption spectroscopy confirmed the formation of a zinc(II) complex with an absorption maximum at 486 nm.[46]

[Zn(α-OMe-4-mecdpm)$_2$] was characterized by a variety of methods including mass spectrometry, NMR, infrared, and electronic spectroscopy. Single crystals were also obtained directly by slow evaporation from the reaction mixture and X-ray structural analysis confirmed the formation of the desired complex (Table 2). Upon examination of the [Zn(α-OMe-4-mecdpm)$_2$] structure, several unusual features not seen in other zinc(II) dipyrrinato complexes were found (Fig. 4).[46] In other zinc(II) dipyrrinato metal complexes the metal ion is approximately tetrahedral with nearly orthogonal dipyrrin ligands. However, the [Zn(α-OMe-4-mecdpm)$_2$] complex adopts a very distorted tetrahedral conformation with a mean interligand dihedral angle of 54.7°. By way of comparison, the interligand dihedral angles found in bis(5-phenyldipyrrinato)zinc(II),[46] which has two independent complexes in the asymmetric unit, are 86.0° and 88.5°. The complex is also twisted so that the two methoxy groups are close to each other, further perturbing the ligand set to give interligand

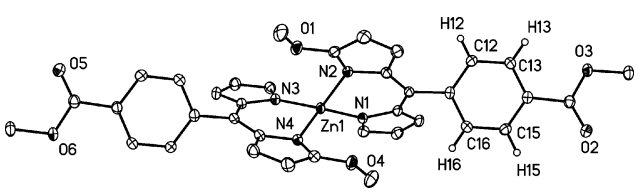


Fig. 4 Structural diagram of [Zn(α-OMe-4-mecdpm)$_2$] with partial atom numbering scheme (ORTEP, 50% probability ellipsoids). Most hydrogen atoms have been omitted for clarity.

angles, N1–Zn–N3 and N2–Zn–N4, of 119° and 99°, respectively (Fig. 5). This distortion of the zinc coordination sphere may be explained in part by the crystal packing, which places the methyl ester moieties near the core dipyrrin ligands. Electronic repulsion between the methyl ester and methoxy moieties could cause the methoxy groups to gather onto one side of the zinc(II) coordination sphere. This arrangement may also be stabilized by a weak hydrogen bond involving the α-carbon of an unsubstituted dipyrrin pyrrole ring and the carbonyl group of a nearby methyl ester. Both influences are shown in Fig. S3.† The dipyrrin moieties of each ligand in [Zn(α-OMe-4-mecdpm)$_2$] are nearly planar with torsion angles of 7.4° and 6.3°, which is closer to planarity than the free ligand, but more distorted than reported in other dipyrrinato complexes.[16,43,45,47,48]

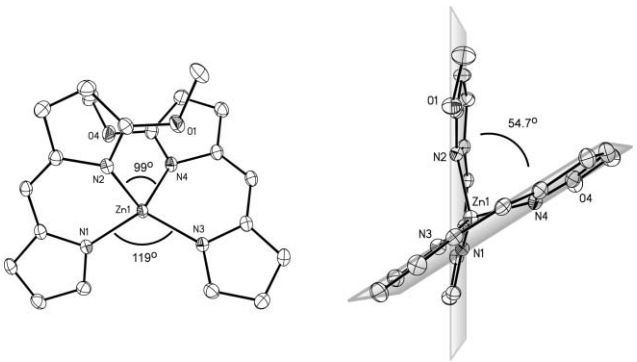


Fig. 5 [Zn(α-OMe-4-mecdpm)$_2$] metal core with partial atom numbering schemes (50% probability ellipsoids) viewed along two different off-axis directions. The *meso*-phenyl ring and hydrogen atoms have been removed for clarity. The coordination sphere shows an unusual *cis* geometry and distortion away from an idealized tetrahedral geometry.

Solution dynamics of [Zn(α-OMe-4-mecdpm)$_2$]

Upon close examination of the ^{1}H NMR spectrum of [Zn(α-OMe-4-mecdpm)$_2$], the resonances associated with the *ortho*-protons, H12 and H16, appear as a doublet of doublets (Fig. 6). This is in contrast to the doublet of the same protons in the free ligand and of other metal dipyrrinato complexes,[16,45–47] and is indicative of the asymmetry of the complex which renders the phenyl protons

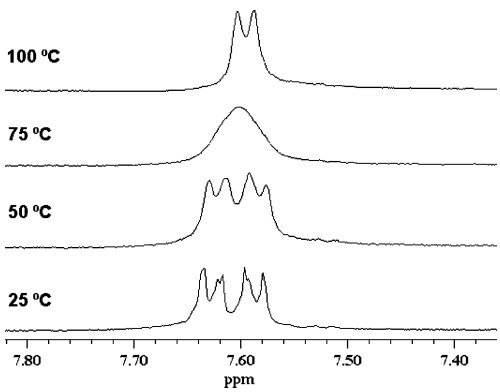


Fig. 6 Variable temperature ^{1}H NMR spectra of the *ortho* protons H12 and H16 (see Fig. 4) of [Zn(α-OMe-4-mecdpm)$_2$] in d^6-DMSO. The resonances coalesce upon heating, indicative of rapid rotation about the dipyrrin–aryl bond.

inequivalent. The chemical inequivalence of these protons was used as a probe to measure the rotation barrier of the aryl group using variable temperature NMR (Fig. 6). As the temperature is increased the doublets of H12 and H16 coalesce at a $T_c \approx$ 86 °C (359 K). This corresponds to a free energy of activation of $\Delta G^{\ddagger} = 17.3$ kcal mol^{-1} for rapid rotation about the dipyrrin–aryl bond.[49] The phenyl protons H13 and H15, (Fig. 4) also undergo a less pronounced splitting, which coalesce at elevated temperatures. Similar phenyl proton coalescence has been reported when *meso*-tetraphenylporphyrinato (TPP) complexes and *para*-substituted TPP complexes have asymmetric axial ligation to the central metal atom.[50–53] For those compounds, the free energy of activation was measured to be between 12.8 and 18.6 kcal mol^{-1}, with electron-withdrawing *para* substituents, such as trifluoromethyl groups, leading to the higher barriers. The aryl rotation barrier for [Zn(α-OMe-4-mecdpm)$_2$] of 17.3 kcal mol^{-1} lies toward the higher end of this range and might reflect the influence of the *para*-methyl ester substituent. To our knowledge, this is the first time that such aryl rotation has been experimentally observed in a *meso*-aryl dipyrrinato complex.

Conclusions

While symmetrically-substituted α,α′-thioalkyl dipyrrins[54] and asymmetrically-substituted α-methoxy dipyrrins[55] recently have been prepared from 2-thiocyanatopyrrole or pyrrolin-2-one precursors, respectively, the present work represents the first asymmetrically-substituted α-alkoxy dipyrrins that have been synthesized directly from dipyrrins lacking substituents in the α-positions. This methodology has now been applied to reactions with a variety of alcohols and 5-(aryl)dipyrrins. Several compounds, including Mn(OAc)$_2$·4H$_2$O, FeCl$_3$·6H$_2$O, and Na$_3$Co(NO$_2$)$_6$ were found to promote the reaction, and the presence of a hydroquinone has proven vital for the formation of the products under these reaction conditions. The synthesis of both hetero- and homoleptic metal complexes has been described and their structures have been probed both in solution and in the solid state. The potential utility of this synthetic methodology will be realized by further optimization of reaction conditions.

Experimental

General methods

Unless otherwise noted, starting materials were obtained from commercial suppliers and used without further purification. Pyrrole was freshly distilled prior to use. ^{1}H/^{13}C NMR spectra were recorded on a Varian FT-NMR spectrometer running at 400 MHz or a Unity FT-NMR spectrometer running at 500 MHz at the Department of Chemistry and Biochemistry, University of California, San Diego. Infrared spectra were collected on a Mattson Research Series FT-IR instrument (using NaCl plates, laboratory of Prof. Clifford P. Kubiak) at the Department of Chemistry and Biochemistry, University of California, San Diego. UV-Visible spectra were recorded using a Perkin-Elmer Lambda 25 spectrophotometer with the UVWinLab 4.2.0.0230 software package. Mass spectra were acquired at the Small Molecule Mass Spectrometry Facility located in the Department of Chemistry and Biochemistry, University of California, San Diego. A

ThermoFinnigan LCQ-DECA mass spectrometer was used for ESI and APCI analysis, and the data were analyzed using the Xcalibur software suite. A ThermoFinnigan MAT 900XL mass spectrometer was used to acquire the data for the high resolution mass spectra (HRMS).

Syntheses

[5-(4-Cyanophenyl)-1-methoxy-4,6-dipyrrinato]bis[5-(4-cyanophenyl)-4,6-dipyrrinato]cobalt(III), [Co(α-OMe-4-cydpm)(4-cydpm)$_2$]. 5-(4-Cyanocarbonylphenyl)-4,6-dipyrromethane[39] (0.20 g, 0.81 mmol) was dissolved in 150 mL $CHCl_3$ and stirred in an ice bath. DDQ (0.20 g, mmol) was dissolved in benzene (150 mL) and added slowly dropwise. The solvent was then evaporated and the resulting dark residue was redissolved in a 1 : 1 mixture of $CHCl_3$/MeOH (100 mL). $Na_3Co(NO_2)_6$ (0.11 g, 0.27 mmol) dissolved in a 1 : 1 mixture of H_2O/MeOH (6 mL) was added. Triethylamine (1 mL) was added to the solution. The resulting mixture was heated to 70 °C overnight. The solution was evaporated to dryness and the product was purified by column chromatography (SiO_2; 3:2 to 9 : 1 CH_2Cl_2 : hexanes) to afford three products: α-OMe-4-cydpm (yellow film, 0.064 g, 32% yield), Co(4-cydpm)$_3$[17] (orange solid, 0.070 g, 33% yield), and Co(α-OMe-4-cydpm)(4-cydpm)$_2$ (red solid, 0.060 g, 27% yield).

Co(α-OMe-4-cydpm)(4-cydpm)$_2$. ^{1}HNMR ($CDCl_3$ 400 MHz, 25 °C): δ 3.41 (s, 3H), 6.00 (d, 1H, $J = 4.8$ Hz), 6.20–6.44 (m, 7H), 6.50 (s, 1H), 6.55 (d, 1H, $J = 4.8$ Hz), 6.57–6.62 (m, 4H), 6.63 (d, 2H, $J = 4.4$ Hz), 6.75 (s, 1H), 6.94 (s, 1H), 7.43 (t, 2H, $J = 8.8$ Hz), 7.49–7.62 (m, 4H), 7.68 (d, 2H, $J = 8.8$ Hz), 7.73–7.77 ppm (m, 4H). APCI-MS: m/z 821.85 $[M + H]^+$. HR-FABMS: m/z 822.2146 $[M + H]^+$ (Calcd m/z 822.2135). λ_{max} (CH_2Cl_2 solution): 266, 304, 408, 493 nm. IR (thin film CH_2Cl_2): ν 2926, 2857, 2229, 1566, 1381, 1347, 1249, 1033, 998, 812 cm^{-1}.

5-(4-Cyanophenyl)-1-methoxy-4,6-dipyrromethene, α-OMe-4-cydpm. 5-(4-Cyanophenyl)-4,6-dipyrromethane[39] (0.20 g, 0.81 mmol) was dissolved in 100 mL $CHCl_3$ and stirred in an ice bath. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (0.18 g, 0.81 mmol) was dissolved in 100 mL benzene and added dropwise over ~1 h. After addition, the reaction mixture was then evaporated to dryness and the resulting dark residue was redissolved in 25 mL MeOH and 25 mL $CHCl_3$. $Na_3Co(NO_2)_6$ (0.11 g, 0.27 mmol) dissolved in 2 mL H_2O and 1 mL MeOH was added to the solution. The resulting mixture was heated to reflux while stirring overnight. The solution was evaporated to dryness and the product was purified by column chromatography (SiO_2; 4 : 1 CH_2Cl_2 : hexanes) to afford a yellow solid. Yield: 18% (0.041 g). ^{1}HNMR ($CDCl_3$ 400 MHz, 25 °C): δ 4.14 (s, 3H), 6.02–6.11 (m, 1H), 6.19 (d, 1H, $J = 4.4$ Hz), 6.20–6.27 (m, 1H), 6.62 (d, 1H, $J = 4.4$ Hz), 7.17 (bs, 1H), 7.56 (d, 2H, $J = 8.0$ Hz), 7.72 (d, 2H, $J = 8.0$ Hz), 12.11 ppm (bs, 1H, NH). ^{13}CNMR ($CDCl_3$ 100 MHz, 25 °C): δ 56.0, 110.3, 112.0, 117.4, 117.8, 118.4, 124.6, 131.0, 131.3, 131.6, 136.9, 141.9, 143.6, 175.3 ppm. APCI-MS: m/z 276.117 $[M + H]^+$. HR-FABMS: m/z 275.1054 $[M]^+$ (calcd m/z 275.1053). λ_{max} (CH_2Cl_2 solution): 264, 285, 407 nm. IR (thin film CH_2Cl_2): ν 2936, 2229, 1598, 1557, 1532, 1406, 1377, 1290, 1122, 1089, 1041, 937, 804, 775, 746, 691 cm^{-1}.

5-(4-Methoxycarbonylphenyl)-1-methoxy-4,6-dipyrromethene, α-OMe-4-mecdpm. The same procedure was used as in the synthesis of α-OMe-4-cydpm, starting from 5-(4-methoxycarbonylphenyl)-4,6-dipyrromethane[48] (0.20 g, 0.71 mmol) to afford a yellow film. Yield: 19% (0.043 g). ^{1}HNMR ($CDCl_3$ 400 MHz, 25 °C): δ 3.96 (s, 3H), 4.13 (s, 3H), 6.11 (bd, 1H, $J = 3.2$ Hz), 6.17 (d, 1H, $J = 4.8$ Hz), 6.21 (bt, 1H, $J = 3.2$ Hz), 6.68 (d, 1H, $J = 4.4$ Hz), 7.15 (bs, 1H), 7.53 (d, 2H, $J = 8.4$ Hz), 8.10 (d, 2H, $J = 8.4$ Hz), 12.15 ppm (bs, 1H, NH). ^{13}CNMR ($CDCl_3$ 100 MHz, 25 °C): δ 52.2, 55.9, 110.3, 117.3, 117.7, 124.5, 128.8, 129.9, 130.8, 132.2, 132.4, 137.5, 142.0, 143.7, 166.8, 175.3 ppm. ESI-MS: m/z 309.15 $[M + H]^+$. HR-FABMS: m/z 309.1239 $[M + H]^+$ (calcd m/z 309.1234). λ_{max} (CH_2Cl_2 solution): 289, 407 nm. IR (thin film CH_2Cl_2): ν 3446, 2950, 1713, 1598, 1557, 1545, 1406, 1392, 1376, 1288, 1276, 1115, 1090, 1041, 764, 745, 718 cm^{-1}.

5-(4-Methoxycarbonylphenyl)-1-ethoxy-4,6-dipyrromethene, α-OEt-4-mecdpm. The same procedure was used as in the synthesis of α-OMe-4-cydpm, starting from 5-(4-methoxycarbonylphenyl)-4,6-dipyrromethane[48] (0.20 g, 0.71 mmol) and ethanol (10 mL). Yield: 35% (0.081 g). ^{1}HNMR ($CDCl_3$ 400 MHz, 25 °C): δ 1.50 (t, 3H, $J = 7.2$ Hz), 3.96 (s, 3H), 4.53 (q, 2H, $J = 7.6$ Hz, $J = 6.8$ Hz), 6.11 (bd, 1H, $J = 3.6$ Hz), 6.16 (d, 1H, $J = 4.4$ Hz), 6.21 (bs, 1H), 6.67 (d, 1H, $J = 4.8$ Hz), 7.14 (bs, 1H), 7.53 (d, 2H, $J = 8.8$ Hz), 8.10 (d, 2H, $J = 8.4$ Hz), 12.14 ppm (bs, 1H, NH). ^{13}CNMR ($CDCl_3$ 100 MHz, 25 °C): δ 14.5, 52.2, 64.6, 110.2, 117.5, 117.6, 124.3, 128.8, 129.9, 130.8, 132.1, 132.2, 137.3, 142.0, 143.9, 166.8, 174.7 ppm. ESI-MS: m/z 323.05 $[M + H]^+$. HR-FABMS: m/z 323.1388 $[M + H]^+$ (calcd m/z 323.1390). λ_{max} (CH_2Cl_2 solution): 290, 407 nm. IR (thin film CH_2Cl_2): ν 3446, 3301, 2976, 2950, 1724, 1597, 1549, 1531, 1406, 1392, 1378, 1346, 1286, 1257, 1112, 1090, 1039, 764, 741, 724 cm^{-1}.

5-(4-Methoxycarbonylphenyl)-1-propoxy-4,6-dipyrromethene, α-OPr-4-mecdpm. The same procedure was used as in the synthesis of α-OMe-4-cydpm, starting from 5-(4-methoxycarbonylphenyl)-4,6-dipyrromethane[48] (0.20 g, 0.71 mmol) and propanol (10 mL). Yield: 38% (0.091 g). ^{1}HNMR ($CDCl_3$ 400 MHz, 25 °C): δ 1.09 (t, 3H, $J = 7.6$ Hz), 1.82–1.98 (m, 2H), 4.43 (t, 2H, $J = 6.4$ Hz), 6.11 (bd, 1H, $J = 3.2$ Hz), 6.18 (d, 1H, $J = 4.8$ Hz), 6.21 (bs, 1H), 6.68 (d, 1H, $J = 4.8$ Hz), 7.15 (bs, 1H), 7.53 (d, 2H, $J = 8.4$ Hz), 8.10 (d, 2H, $J = 8.0$ Hz), 12.16 ppm (bs, 1H, NH). ^{13}CNMR ($CDCl_3$ 100 MHz, 25 °C): δ 10.5, 22.2, 52.1, 70.3, 110.1, 117.5, 117.6, 124.3, 128.8, 129.8, 130.8, 132.0, 132.2, 137.2, 142.0, 143.9, 166.7, 174.9 ppm. FAB-MS: m/z 336.2 $[M]^+$. HR-FABMS: m/z 336.1459 $[M]^+$ (calcd m/z 336.1468). λ_{max} (CH_2Cl_2 solution): 289, 407 nm. IR (thin film): ν 3278, 2964, 2953, 2881, 1725, 1597, 1549, 1532, 1407, 1364, 1338, 1286, 1279, 1101, 1091, 1040, 960, 763, 742, 725 cm^{-1}.

Bis[5-(4-methoxycarbonylphenyl)-1-methoxy-4,6-dipyrrinato]-zinc(II), [Zn(α-OMe-4-mecdpm)$_2$]. α-OMe-4-mecdpm (0.172 g, 0.558 mmol) was dissolved in 25 mL of $CHCl_3$ and 25 mL of MeOH. $Zn(OAc)_2 \cdot 2H_2O$ was dissolved in 5 mL of MeOH and added to the solution. Triethylamine (0.5 mL) was added and the reaction was stirred overnight at room temperature. The solution was then slowly evaporated to yield bright orange crystals, which were washed 3 times with 5 mL of MeOH. Yield: 77% (0.146 g). ^{1}HNMR ($CDCl_3$ 400 MHz, 25 °C): δ 3.76 (s, 6H), 3.98 (s, 6H), 6.00 (d, 2H, $J = 4.4$ Hz), 6.33 (d, 2H, $J = 4.4$ Hz), 6.41 (d, 2H, $J = 3.6$ Hz), 6.65 (d, 2H, $J = 4.4$ Hz), 7.37 (s, 2H), 7.60 (q, 4H, $J = 5.2$ Hz, $J = 7.6$ Hz), 8.04–8.20 (m, 4H). ^{13}CNMR ($CDCl_3$

Table 2 Summary of X-ray structural parameters

	α-OMe-4-cydpm	[Zn(α-OMe-4-mecdpm)$_2$]
Empirical formula	$C_{17}H_{13}N_3O$	$C_{36}H_{30}N_4O_6Zn$
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	8.8386(9)	11.9083(7)
b/Å	9.3207(9)	11.9234(7)
c/Å	10.0246(10)	12.0192(7)
α/°	63.7840(10)	69.4180(10)
β/°	68.1580(10)	88.6430(10)
γ/°	78.077(2)	78.7560(10)
V/Å^3, Z	686.82(12), 2	1565.77(16), 2
Crystal size/mm	0.30 × 0.17 × 0.15	0.40 × 0.19 × 0.15
T/K	100(2)	100(2)
Reflections collected	5831	13652
Independent reflections	2979, R(int) = 0.0182	6804, R(int) = 0.0155
Data/restraints/parameters	2979/0/195	6804/0/428
Goodness-of-fit on F^2	1.066	1.025
Final R indices $I > 2\sigma(I)$	$R1 = 0.0455$, $wR2 = 0.1228$	$R1 = 0.0293$, $wR2 = 0.0777$
R indices (all data)	$R1 = 0.0507$, $wR2 = 0.1272$	$R1 = 0.0310$, $wR2 = 0.0791$

100 MHz, 25 °C): δ 52.3, 57.4, 103.9, 114.2, 127.4, 128.2, 128.3, 129.7, 130.7, 130.8, 134.1, 136.9, 138.1, 142.2, 143.5, 144.0, 166.7, 171.8. FAB-MS: m/z 678.4 [M]$^+$. HR-FABMS: m/z 678.1437 [M]$^+$ (calcd m/z 678.1451). λ_{max} (CH_2Cl_2 solution): 306, 486 nm. IR (thin film CH_2Cl_2): ν 3012, 3050, 2951, 2926, 2846, 1723, 1556, 1508, 1497, 1404, 1379, 1346, 1318, 1276, 1269, 1194, 1113, 1048, 1005, 962, 829, 763, 725 cm^{-1}.

Crystallography

Single crystals of each compound suitable for X-ray diffraction structural determination were mounted on quartz capillaries or nylon loops by using Paratone oil and were cooled in a nitrogen stream on the diffractometer. For further details see ESI† and Table 2.

CCDC reference numbers 624663 and 624664.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b615801c

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