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Asymmetric Synthesis of Mono- and Dinuclear Bis(dipyrrinato) Complexes

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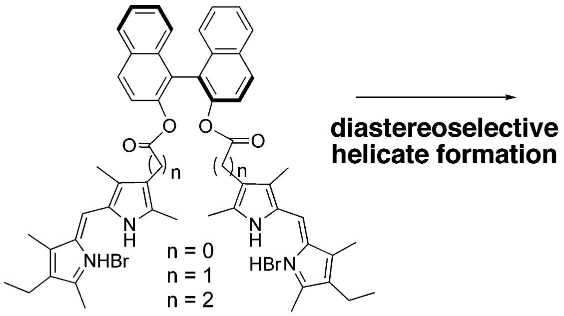

The diastereoselective syntheses of Zn(II) bis(dipyrrinato) helicates is reported, involving ligands templated by the incorporation of homochiral binol within the linker joining the two dipyrrinato units. The most diastereoselective formation of dinuclear bis(dipyrrinato) helicates to date is reported. The formation of either mononuclear or dinuclear helicates can be tuned by varying the length of the linker between the dipyrrinato units and by varying the complexation procedure. The neutral dipyrrinato helicates were readily analyzed by HPLC to ascertain diastereoselectivity, and circular dichroism studies revealed the helical nature of the complexes. The molar ellipticities of the helicates produced by diastereoselective complexation are very large in the visible region and typically correspond to binol moieties in the UV region. Extensive X-ray crystallographic investigations further confirmed the helicity of the mononuclear Zn(II) helicates and identified significant interlayer displacement and bending within crystals.

Introduction

Metal-ion assisted self-assembly is a useful strategy for the preparation of helical architectures, and polybipyridyl ligands have been used extensively for this purpose.[1−3] Being neutral, bipyridyl ligands generate complexes bearing the charge of the metal ion to which they are coordinated. In contrast, dipyrrins (dipyrromethenes)[4] (Figure 1) give monoanionic, planar, fully conjugated bidentate ligands for chelation with metal ions[5,6] and with $^{+}BR_2$. Indeed, $^{+}BF_2$ complexes of dipyrrins constitute the fluorescent BODIPY dyes extensively used as probes and sensors.[7] Neutral complexes of dipyrrins can often be purified by flash chromatography and analyzed by HPLC.[8−11] Dipyrrins,

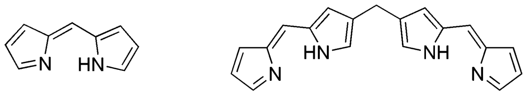

FIGURE 1. Skeletal dipyrrin and 2,2′-bis(dipyrrin).

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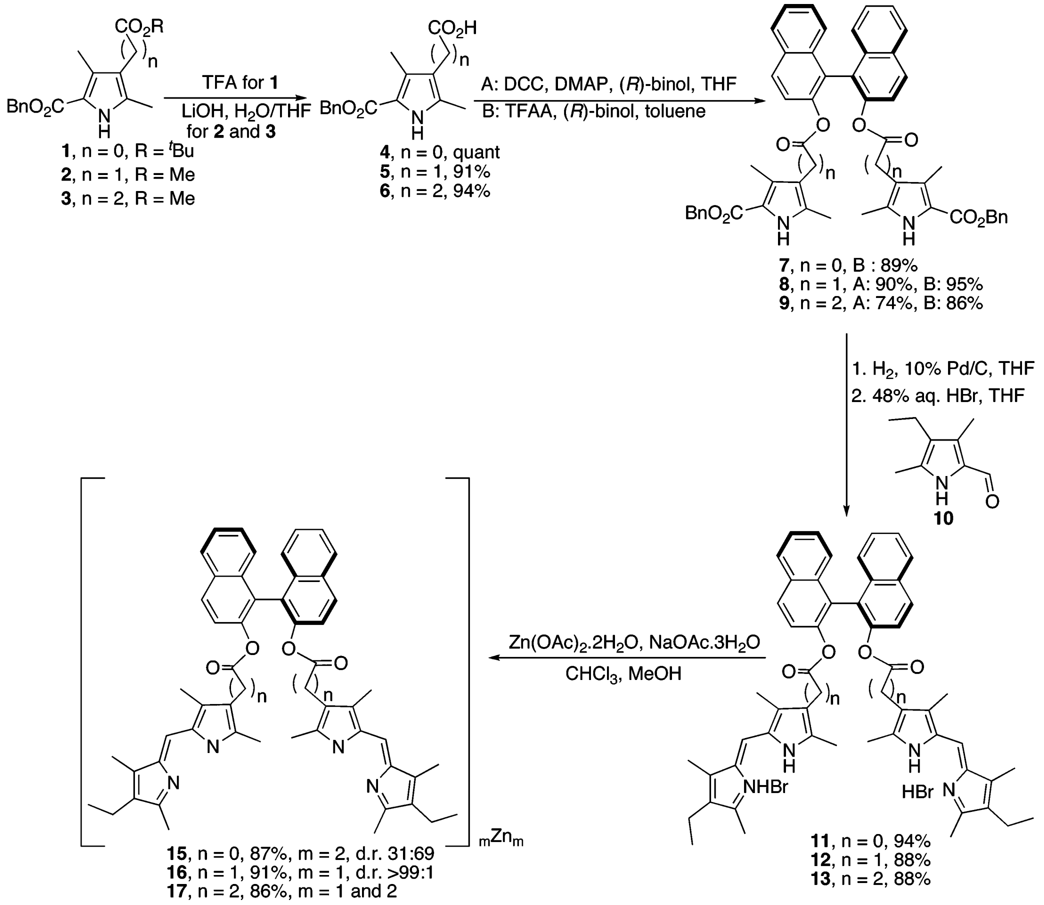

FIGURE 2. Templated synthesis of Zn(II) bis(dipyrrinato) complexes.

including highly functionalized derivatives, are readily prepared from the corresponding pyrrole(s) and can usually be stored indefinitely as their crystalline hydrobromide salts.[12]

The nuclearity and pitch of helicates formed using 1,1′- and 2,2′-bis(dipyrrin)s[4] is dependent upon the length and nature of the linker joining the two dipyrrinato units, as well as the coordination geometry requirements of the metal ion.[13] Bröring separated nickel(II) 2,2′-bis(dipyrrinato) helicates using MPLC, thereby demonstrating the stereochemical stability of the helicates.[11] Appending chirality onto the bis(dipyrrin) potentially gives rise to diastereoisomeric helicates and thus the opportunity for asymmetric complexation. We previously reported the first synthesis of dinuclear zinc(II) bis(dipyrrinato) helicates featuring bis(dipyrrins)s bearing pendent homochiral amides and esters.[8,14] The CD-spectra of the reaction mixtures for complexation showed measurable ellipticities, indicating that the complexation had occurred diastereoselectivity. However, the extent of diastereoselectivity was very low ($<$10%), as determined using NMR spectroscopy. The inclusion of a homochiral moiety within the linker joining two dipyrrin units provides potential for the linker to act as a chiral template for complexation; following a preliminary communication,[9] full results of using binol as a homochiral templating unit are hereby reported.

Results and Discussion

To examine the potential for templated diastereoselective complexation of bis(dipyrrin)s, a homochiral binol moiety was incorporated into the linker joining two dipyrrin units, and three such ligands were synthesized with varying linker length (Figure 2). Hydrolysis of the Knorr-type pyrrole carboxylates **1**−**3**, followed by coupling of the resultant carboxylic acids **4**−**6** with (*R*)-binol gave the dipyrroles **7**−**9**. Although coupling in the presence of DCC and DMAP gave good yields of **8** and **9**, the purification of the bipyrroles was extremely tedious, owing to the presence of dicyclohexylurea as byproduct, and required repeated flash chromatography. An alternative coupling procedure involving TFAA[15] gave excellent yields and required only a simple isolation procedure; consequently, this coupling strategy was used for the preparation of **7**. Hydrogenative debenzylation of **7**−**9**, followed by acid-catalyzed decarboxylation, gave the corresponding α-free dipyrroles which were condensed in-situ with 4-ethyl-2-formyl-3,5-dimethyl-pyrrole (**10**) to furnish the required bis(dipyrrin)s as their hydrobromide salts **11**−**13**. The enantiomeric bis(dipyrrin) (**14**) of the ethanoate derivative **12** was prepared using (*S*)-binol.

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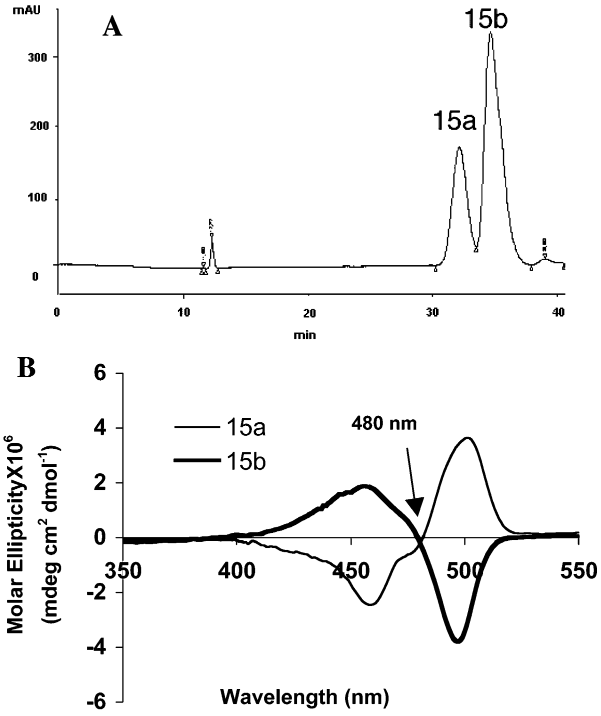

FIGURE 3. (A) HPLC trace with resolved **15a** and **15b**, CHIRALPAK IA, CH_3OH/CH_3CN (60:40), 1 mL min^{-1}, ambient temperature. (B) Superimposed molar ellipticity of **15a** and **15b**, $CH_3OH/CHCl_3$ (98:2): λ_{489nm} **15a**, ϵ 440000 L mol^{-1} dm^{-1}; $[\Theta]_{490nm}$ **15a**, 3.7 × 10^6 deg cm^2 dmol^{-1}; λ_{490nm} **15b**, ϵ 460000 L mol^{-1} dm^{-1}; $[\Theta]_{497nm}$ **15b**, −3.8 × 10^6 deg cm^2 dmol^{-1}.

Cognizant that coordination of unsymmetrical bis(dipyrrin)s with tetrahedral metal ions gives helicates, and with the goal of investigating the effects of the planar chiral binol moiety upon the diastereoselectivity of complexation, ligands **11**−**13** were reacted with $Zn(OAc)_2$ according to standard conditions (Figure 2).[14] HPLC and NMR spectroscopy were used to analyze the crude reaction mixtures, and mass spectrometry enabled the identification of monomeric and dimeric oligomers. Although helicates bearing point-chiral appendages are formally diastereoisomeric, separation of neither oligomers nor diastereoisomers was possible by flash chromatography on silica or alumina. However, as the gross helicity of the bis(dipyrrinato) complexes renders the isomers pseudoenantiomeric, a chiral column (CHIRALPAK IA) and HPLC proved to be most effective for the resolution of the diastereoisomers and also allowed resolution of monomeric and dimeric oligomers.

HPLC analysis of the crude reaction mixture from the Zn(II) complexation of methanoate derivative **11** indicated the presence of two dipyrrinato complex isomers (**15a** and **15b**, as eluted) in a ratio of 31:69 (Figure 3A). Separation of the resolved isomers by preparative chiral HPLC and subsequent mass spectrometry confirmed the formation of two diastereoisomeric dinuclear complexes, $Zn_2[bis(dipyrrinato)]_2$. The separated diastereoisomers, both of which were fully characterized, were found to exhibit approximately opposite ellipsoidal circular dichrioism (CD) spectra (Figure 3B), as anticipated for pseudoenantiomeric helicates whereby the helical chirality stems from the dipyrrinato units and not from the point-chiral auxiliary.[16] Diastereoisomer **15a**, which exhibited a positive ellipticity at 501 nm, was assigned as the *M*-helix and similarly **15b** was assigned as the *P*-helix.[8,9,11,17] This work represents the most diastereoselective complexation reported so far for the synthesis of dinuclear bis(dipyrrinato) double helicates (dr = 31:69, de = 38%).

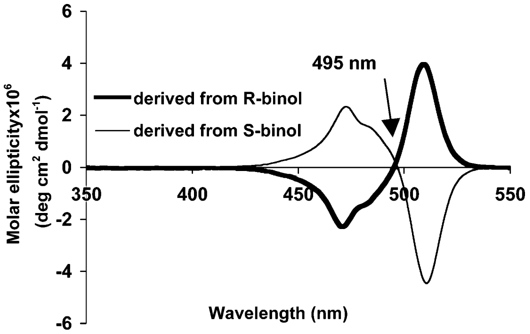

FIGURE 4. Molar ellipticity for Zn(II) helicates of **12** (*R*-binol derived) and **14** (*S*-binol derived), $CH_3OH/CHCl_3$ (98:2), λ_{474nm} ϵ 124000 L mol^{-1} dm^{-1}; $[\Theta]_{511nm}$ −4.5 × 10^6 deg cm^2 dmol^{-1} for the *S*-derived complex.

The ethanoate-linked bis(dipyrrin) **12** gave only a single isomer (**16**) upon coordination to Zn(II) (Figure 2), as determined by NMR spectroscopy and HPLC.[9] Interestingly, the mass spectrum for this complex indicated a mononuclear structure, Zn[bis(dipyrrinato)], and so increasing the length of the linker by two atom units (**11** cf. **12***)* dramatically altered the outcome of complexation in terms of both the nuclearity of the product and the diastereoselectivity, thereby highlighting the reliance of product outcome on ligand structure. Analysis using CD showed that **16** and the Zn(II) complex prepared from the enantiomeric ligand (**14**, incorporating (S)-binol) exhibited, as expected for pseudoenantiomeric helicates, equal and opposite molar ellipticities (Figure 4). By correlation,[8,9,11,17] the complex derived from (*R*)-binol was assigned as the *M*-helicate (later confirmed by X-ray crystallography), and the complex derived from (*S*)-binol was assigned as the *P*-helicate. The Co(II) complex of **12** was also formed as a single diastereoisomeric *M*-helicate according to mass spectrometry, HPLC, and CD. These complexations are the most diastereoselective (>99.5%) reported for the synthesis of dipyrrinato helicates. Furthermore, the molar ellipticities of the pure mononuclear helicates are remarkably high in the visible region with the molar ellipticities for the binol unit being consistent in the UV range.

To further study the effect upon complexation of increasing the linker length between the two dipyrrin units, the propanoate derivative (**13**) was reacted with $Zn(OAc)_2$ (Figure 2). As for all the complexation reactions, the corresponding complexes were obtained in excellent yield. Analysis of the reaction mixture by chiral HPLC revealed two major isomers in a ratio of 33:67. After separation, the first-eluted isomer (**17a**) was determined by mass spectrometry to be a mononuclear bis(dipyrrinato) complex. By correlation to the pure *M*-helical Zn(II) complex **16** and previous reports,[8,9,11,17] CD analysis (Figure 5) confirmed that the monomer **17a** adopted *M*-helicity.

Initially, the use of mass spectrometry (ESI$^+$, EI$^+$, and MALDI) did not determine a molecular ion for **17b** and instead only the free-base of ligand **13** was detected. Presumably, the ionization conditions caused decomplexation since CD, UV−

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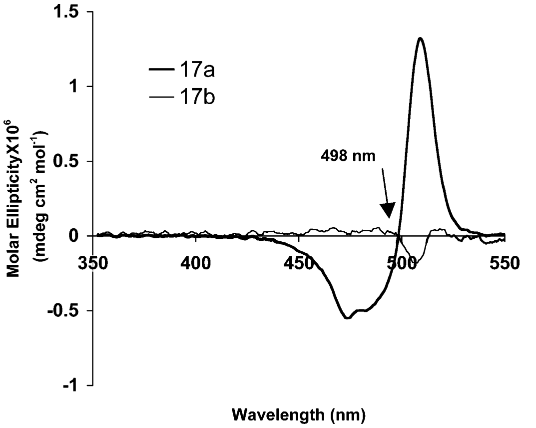

FIGURE 5. Molar ellipticity for purified complexes mononuclear **17a** and dinuclear **17b**, $CH_3OH/CHCl_3$ (98:2): λ_{501nm} **17a**, ϵ 93500 L mol^{-1} dm^{-1}; $[\Theta]_{509nm}$, 1.3×10^6 deg cm^2 dmol^{-1}; λ_{503nm} **17b**, ϵ 278400 L mol^{-1} dm^{-1}; $[\Theta]_{507nm}$ **17b**, -1.8×10^5 deg cm^2 dmol^{-1}.

TABLE 1. Factors Affecting Mononuclear to Dinuclear (17a/17b) Helicate Ratios

entry	concentration Zn(II) M	concentration **13** M	Zn(II)/L	**17a**/**17b**
1	0.09	0.01	9:1	1:2
2	0.01	0.01	1:1	3.2:1
3	8.0×10^{-4}	8.0×10^{-4}	1:1	4:1

vis spectroscopy, and NMR spectroscopy all indicated the presence of bis(dipyrrinato) complex(es), rather than free-base. The weak aryl−metal complexation between silver ions and dipyrrins has previously been useful for chiral lanthanide shift NMR analysis of bis(dipyrrinato) helicates.[18] To enhance the ionization and mass spectrometric detection of **17b**, silver ions in the form of silver trifluoroacetate were used to enhance cationization[19] (1:1 **17b**/$AgCO_2CF_3$ solution in methanol). The ESI^+ detection of the Ag^+ adduct indicated **17b** to be the dinuclear Zn(II) complex of ligand **13**, and this method of cationization is proving to be a generally useful method for the ESI^+ analysis of dipyrrinato complexes in our laboratory.

Overall, complexation of **13** led to a mixture of mononuclear and dinuclear complexes, **17a** and **17b**, in a 1:2 ratio, respectively. The mononuclear isomer **17a** was formed distereomerically pure, as determined by HPLC and NMR spectroscopy, whereas dinuclear **17b** was formed as a mixture of diastereoisomers that were not totally resolvable. The molar ellipticities for **17a** and **17b** are shown in Figure 5. Remarkably, the incorporation of a further two atom unit within the linker (**12** cf. **13***)* results in a mixture of mononuclear and dinuclear complexes of **13** versus a single mononuclear complex of **12**, and further highlights the acute reliance of oligomeric formation on bis(dipyrrin) ligand structure.

To enhance the formation of one oligomeric complex of **13** over the other, the reaction concentration and stoichiometry ratio were varied in 1:1 $MeOH/CHCl_3$, and HPLC analysis was used to assess the product outcome (Table 1) as the mononuclear and dinuclear isomers were well resolved. Decreasing the stoichiometry of Zn(II)/**13** from 9:1 to 1:1 led to a reversal in the selectivity and predominance of the mononuclear product **17a** (entries 1 and 2). Furthermore, decreasing the concentration of the complexation reaction mixture also led to an increase in the formation of the mononuclear product (entries 2 and 3).

The results shown in Table 1 were used in the design of a route to pure mononuclear helicate **17a**. Indeed, when a dilute solution of the purified dinuclear complex **17b** was exposed to an acidic solution (1 M HCl in methanol), HPLC analysis confirmed that the free-base ligand was formed as a result of decomplexation. The in-situ addition of triethylamine to the solution containing free-base gave a complex which possessed an identical retention time to the mononuclear complex observed for the purified mononuclear complex **17a** and which exhibited a molecular ion (ESI^+) corresponding to the mononuclear complex. Furthermore, the recomplexed material exhibited CD behavior identical to that of purified **17a**. Thus, the dinuclear complex was completely converted to the mononuclear complex via such decomplexation/recomplexation under dilute conditions.

The mononuclear Zn(II) bis(dipyrrinato) complex of **12** was analyzed by X-ray crystallography. By layering a chloroform solution of **16** with methanol (1:5), single crystals suitable for X-ray diffraction studies were obtained. The preliminary structure of **16** has been previously reported.[9] At that time the data collection on a series of crystals gave ambiguous results. While all provided a subcell close to that reported here, many crystals also satisfied either (or both of) a much larger cell with many missing reflections and/or a cell where two angles were clearly 90° but the third angle was close to 90° but significantly different from it: these are classic symptoms for a twinned crystal. The crystals themselves, generally thin plates, were very fragile, and when manipulated in some directions they shattered into a multitude of small crystals. However, the original crystals were surprisingly plastic, simply bending when manipulated in another direction. Furthermore, the bent crystals could be straightened with apparently no loss to the external crystal form. The systematic absences for the subcell with the data for the preliminary structure suggested either space group $P2_12_12_1$, $P2_12_12$, $P222_1$, or (if monoclinic) $P2_1$. The absences for two of the axial zones thus depended on a judgment call on whether the $2n + 1$ reflections were really all absent. Interestingly the structure could be solved in all four space groups and refined (with some restraints and the removal of a small number of "miss-measured" reflections) to R factors in the low teens. In all cases the molecular structure was clearly visible: approximately the same structure for each space group (two unique molecules for $P2_1$), but the correct structure in the correct space was not properly identified; we report here the resolution of these problems.

The data were next collected on an imaging plate RAXIS RAPID. The cylindrical geometry and wide aperture of this system allowed the rotation geometry of the crystal to be examined in detail. It then became clear that the larger cells, previously detected, were not the result of twinning but rather the consequence of slight displacements of portions of a single crystal, with the displacements occurring preferentially in certain zones. These data also suggested that the angles, previously observed only to be close to 90°, could be the result of certain reflections being elongated by slight displacements in the crystal and thus the centers of some reflections were slightly displaced from their true positions.

Further crystal samples of **16** were examined, this time taking care to select only small, well-formed crystals that had no previous history of manipulation. Several crystals had to be selected until one was found that gave a clear cell, with little

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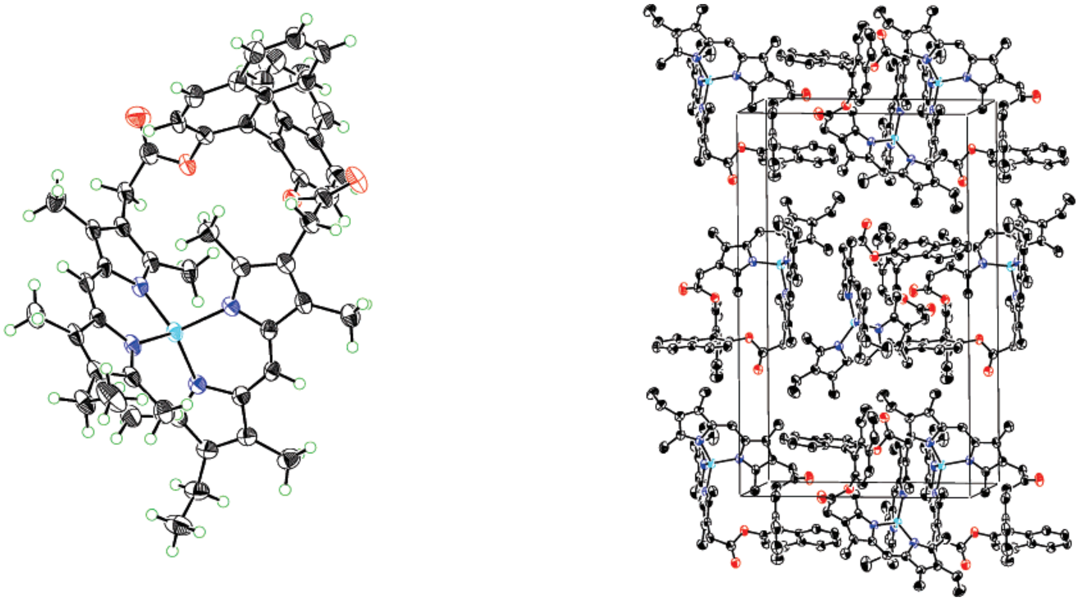

FIGURE 6. ORTEP for **16** and corresponding packing diagram for the unit cell (50% probability ellipsoids).

evidence of displacements having occurred. The structure from this crystal solved quickly and tidily in space group $P2_12_12_1$ and refined to $R = 4.6\%$ without restraints or any other manipulation of the reflection data. The structure, solved in $P2_1$ and then examined by PLATON,[20] reported 98% in $P2_12_12_1$. The absolute configuration of **16** was clearly determined as the *M*-helix with a Flack parameter of 0.012(3), consistent with the configuration assigned using CD data and conformational analysis.[9]

An examination of the completed structure (Figure 6) reveals the source of the difficulties that had been originally encountered. A packing diagram of the unit cell shows that the molecules are arranged in such a way that, although there are interactions between molecules in a layer, there is a wide gap between the layers where there is nothing but H···H contacts to hold the layers in place. This is the classic requirement for crystals that bend,[21] and equally the condition that can cause portions of a crystal to displace on being cut or stressed with the point of a needle; whether the crystal undergoes bending or displacement depends upon the direction of the stress placed upon it. With this knowledge, complexes of bis(dipyrrin)s will be handled with extreme care during future X-ray crystallographic analyses thus minimizing bending and displacement (slipping of layers).

Conclusions

The most diastereoselective syntheses of helical mononuclear Zn(II) bis(dipyrrinato) complexes are reported, using ligands templated by the incorporation of binol within the linker. Increasing the overall length of the linker leads to mononuclear Zn(II) bis(dipyrrinato) helicates with excellent (>99%) diastereoselectivity and the sense of helicity is assigned using circular dichroism and confirmed by X-ray crystallography. Further increase of the length of the linker results in mixtures of mononuclear and dinuclear helicates formed by asymmetric complexation, and the oligomeric selectivity can be tuned by variation of concentration and stoichiometry. Both CD and HPLC were critical to the analysis of all of the asymmetric complexation reactions, and these techniques are applicable to the analysis of dipyrrinato complexes by virtue of the strong chromophoric units within the neutral complexes. Extensive X-ray crystallographic investigations confirmed the helicity of the mononuclear Zn(II) helicates and provided insight into methods that should be used to minimize bending and displacement within crystals of bis(dipyrrin) complexes.

Experimental

Di[benzyl-4,4′-[(*R*)-binolmethanoate-3,5-dimethyl]-1H-pyrrole-2-carboxylate] (7). According to a modification of a reported procedure,[15] to a suspension of carboxylic acid **4**[15] (819 mg, 3.0 mmol) in dry toluene (25 mL) under nitrogen was added trifluoroacetic anhydride (765 mg, 3.6 mmol). The resultant mixture was stirred at room temperature until dissolution of the suspended solute occurred. (*R*)-Binol (430 mg, 1.5 mmol) was added as a solid, and the solution was stirred for 24 h before being diluted with ethyl acetate (25 mL). The mixture was washed with 2 M NaOH (2 × 25 mL) and brine (2 × 25 mL). The organic fraction was dried over Na_2SO_4 and then concentrated in vacuo. The resultant crude product was purified by flash column chromatography eluting with 30% ethyl acetate in hexane to give, upon concentration, the title product as a white powder (1.06 g, 89%); mp 107−109 °C. UV−vis λ_{max}/nm, 276 (ϵ 64400); $[\Theta]_{235}$, -1.89×10^5; δ_H (500 MHz; $CDCl_3$) 9.12 (2H, br s), 7.92 (2H, d, *J* 9.0), 7.86 (2H, d, *J* 8.0), 7.51 (2H, d, *J* 9.0), 7.39 (2H, t, *J* 8.0), 7.22−7.33 (14H, m), 5.19 (4H, s), 2.16 (6H, s), 1.83 (6H, s); δ_C (125 MHz; $CDCl_3$) 162.9, 161.3, 147.0, 140.4, 136.1, 133.9, 132.5, 131.4, 129.0, 128.7, 128.3, 128.1, 128.0, 126.7, 126.2, 125.6, 124.1, 122.7, 117.6, 112.5, 66.0, 13.8, 11.6; *m*/*z* (ESI^+) 819.2 $(M + Na)^+$.

3,3′-[(*R*)-Binolmethanoate]-bis[2,4,dimethyl-5-[(4-ethyl-3,5-dimethyl-1H-pyrrol-2-ylidene)methyl]]-, 1H Pyrrole Dihydrobromide (11). To dipyrrole **7** (319 mg, 0.4 mmol) and 10% Pd on activated carbon (20 mg) under nitrogen was added THF (20 mL). The reaction mixture was exposed to hydrogen at 1 atm and stirred continuously for 15 h. The reaction mixture was filtered through Celite which was then washed with THF (5 mL) and MeOH (5 mL). Removal of the solvents in vacuo from the combined organic

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fractions gave the dicarboxylic acid which was immediately decarboxylated by stirring for 1 h in trifluoroacetic acid (20 mL) at room temperature. To the resultant solution, was added CH_2Cl_2 (25 mL), and the solution was then washed with saturated Na_2CO_3 (2 × 25 mL), added slowly in portions, followed by washing with brine (2 × 25 mL). The organic fraction was dried over Na_2SO_4, and removal of the organic solvent in vacuo gave the α-free dipyrrole. Without further purification, the α-free dipyrrole was dissolved in THF (30 mL) and 4-ethyl-2-formyl-3,5-dimethylpyrrole **(10)** (121 mg, 0.80 mmol), and three drops of concentrated HBr (48%) were added to the mixture. The reaction mixture was stirred at 40 °C for 1.5 h. Removal of the solvent in vacuo, followed by dissolution of the residue in CH_2Cl_2 (40 mL), drying over $MgSO_4$, and removal of the solvent in vacuo gave the crude product. Trituration of the crude solid with diethyl ether gave the title compound as a red/brown powder (358 mg, 94%); mp (dec) > 172 °C. UV−vis λ_{max}/nm, 497 (ϵ 125100); $[\Theta]_{484}$, -7.79×10^5; δ_H (500 MHz; $CDCl_3$) 13.49 (2H, br s), 12.94 (2H, br s), 8.04 (2H, d, *J* 9.0), 7.98 (2H, d, *J* 8.0), 7.50−7.55 (4H, m), 7.34−7.36 (4H, m), 7.08 (2H, s), 2.73 (6H, s), 2.45 (4H, q, *J* 7.5), 2.35 (6H, s), 2.29 (6H, s), 2.13 (6H, s), 1.12 (6H, t, *J* 7.5); δ_C (125 MHz; $CDCl_3$) 161.7, 160.8, 155.5, 146.5, 146.3, 144.5, 133.6, 133.1, 131.5, 129.4, 128.5, 128.2, 127.0, 126.1, 125.9, 124.5, 123.8, 122.2, 120.1, 116.3, 17.2, 14.3, 14.1, 13.3, 11.6, 10.1; *m*/*z* (ESI^+) 795.2 $(MH - 2HBr)^+$.

Zinc Bis[3,3′-[(*R*)-binolmethanoate]-bis[2,4,dimethyl-5-[(4-ethyl-3,5-dimethyl-1H-pyrrol-2-ylidene)methyl]-1H-pyrrolato] (15). To a solution of bis(dipyrrin) hydrobromide salt **11** (382 mg, 0.40 mmol) in $CHCl_3$ (15 mL) was added a solution of $Zn(OAc)_2 \cdot 2H_2O$ (812 mg, 3.7 mmol) and $NaOAc \cdot 3H_2O$ (504 mg, 3.7 mmol) in CH_3OH (15 mL). The reaction mixture was stirred at 40 °C for 2.5 h. Removal of solvent in vacuo, was followed by dissolution of the residue in CH_2Cl_2 (20 mL), washing with H_2O (2 × 10 mL), and drying the organic fraction over $MgSO_4$. Removal of the solvent in vacuo gave the crude product as a film. Trituration of the crude film with hexane gave the title compound as a red/brown powder in a mixture of two diastereoisomeric dinuclear complexes **15a** and **15b** in a 31:69 ratio, respectively, according to chiral HPLC (332 mg, 87%). **15a**: mp (dec) > 255 °C; UV−vis λ_{max}/nm, 489 (ϵ 438800); $[\Theta]_{490}$, 3.65×10^6; δ_H (500 MHz, $CDCl_3$) 7.77 (4H, d, *J* 8.5), 7.45 (2H, d, *J* 8.5), 7.33−7.35 (4H, m), 7.19−7.21 (2H, m), 7.00 (2H, s), 2.40 (6H, s) 2.30 (4H, q, *J* 7.5), 2.25 (6H, s), 1.69 (6H, s), 1.42 (6H, s), 1.01 (6H, t, *J* 7.5); δ_C (126 MHz, $CDCl_3$) 164.3, 163.6, 156.3, 147.7, 140.5, 139.1, 134.3, 134.0, 133.6, 131.3, 129.0, 127.8, 126.5, 125.3, 122.8, 121.5, 115.3, 18.0, 16.7, 15.0, 14.8, 11.8, 10.2; *m*/*z* (ESI^+) 1741.4 $(M+Na)^+$. **15b**: mp (dec) > 271 °C; UV−vis λ_{max}/nm, 490 (ϵ 463500); $[\Theta]_{497}$, -3.84×10^6; δ_H (500 MHz, $CDCl_3$) 7.98 (2H, d, *J* 9.0), 7.94 (2H, d, *J* 8.0), 7.65 (2H, d, *J* 9.0), 7.43−7.46 (4H, m), 7.28 (2H, d, *J* 3.5), 6.82 (2H, s), 2.27 (4H, q, *J* 7.5), 2.09 (6H, s), 2.08 (6H, s), 1.73 (6H, s), 1.41 (6H, s), 0.94 (6H, t, *J* 8.0); δ_C (126 MHz, $CDCl_3$) 163.6, 163.3, 158.5, 147.7, 141.7, 140.3, 139.0, 134.2, 134.0, 133.0, 131.4, 128.8, 128.1, 126.5, 126.4, 125.3, 124.2, 123.4, 122.4, 115.3, 18.0, 16.9, 14.9, 14.8, 11.0, 9.9; *m*/*z* (ESI^+) 1739.3 $(M+Na)^+$.

Zinc Bis[3,3′-(*R*)-binolpropanoate]-bis[2,4,dimethyl-5-[(4-ethyl-3,5-dimethyl-1H-pyrrol-2-ylidene)methyl]-1H-pyrrolato] (17). Following the general procedure as for the preparation of **15**, to a solution of bis(dipyrrin) **13** (319 mg, 0.30 mmol) in $CHCl_3$ (15 mL) was added a solution of $Zn(OAc)_2 \cdot 2H_2O$ (615 mg, 2.80 mmol) and $NaOAc \cdot 3H_2O$ (381 mg, 2.80 mmol) in CH_3OH (15 mL). Workup as before gave the title compound as a red/brown powder (262 mg, 86%) in a 33:67 mixture of mononuclear and dinuclear complexes **17a** and **17b**, respectively, according to chiral HPLC. **17a**: UV−vis λ_{max}/nm, 501 (ϵ 93500); $[\Theta]_{509}$, 1.32×10^6; δ_H (500 MHz, $CDCl_3$) 7.89 (4H, d, *J* 8.5), 7.42 (2H, t, *J* 8.0), 7.20−7.29 (4H, m), 7.08 (2H, d, *J* 9.0), 7.01 (2H, s), 2.66−2.76 (4H, m), 2.35 (4H, q, *J* 7.5), 2.25 (6H, s), 2.24 (6H, s), 2.13−2.18 (4H, m), 1.93 (6H, s), 1.53 (6H, s), 1.02 (6H, t, *J* 7.5); δ_C (125 MHz, $CDCl_3$) 171.4, 156.8, 156.0, 146.9, 137.1, 137.0, 135.8, 135.2, 133.2, 131.3, 129.8, 129.3, 127.9, 126.6, 126.0, 125.6, 124.3, 123.3, 121.9, 120.8 33.4, 20.5, 18.0, 15.0, 14.9, 14.8, 10.0, 9.9; *m*/*z* (ESI^+) 914.3 $(M+2H)^+$. **17b**: UV−vis λ_{max}/nm, 503 (ϵ 278400); $[\Theta]_{507}$, -1.8×10^5; *m*/*z* (ESI^+ using $AgCO_2CF_3$) 1937.6 $(M+Ag+6H)^+$.

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Supporting Information Available: Synthetic procedures and characterization data for new compounds. CCDC 622546 contains the supplementary crystallographic data for this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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