Inorganic Chemistry

Communication

Monohelical Iron(II) and Zinc(II) Complexes of a (1*R*,2*R*)-Cyclohexyl Salen Ligand with Benz[*a*]anthryl Sidearms

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An enantiomerically pure C_2-symmetric salen ligand with benz[*a*]-anthracene siderams produces *M* helical complexes (Fe^{II} and Zn^{II}) in solution. Interconversion to produce a 1:1 mixture of helical conformers in the solid state is possible, despite overlapped sidearms.

Monohelices with chiral ligands are of particular interest due to their high asymmetry, well-defined reaction centers, and potential as asymmetric catalysts.[1] Single-stranded monohelices are synthetically challenging targets since flexible multidentate ligands often prefer to bridge metal centers and produce helicates.[2] We recently reported monohelical salen complexes constructed from rigid phenathryl sidearms attached to a helix-directing 1,1′-binaphthyl backbone.[3] Herein we detail a new, more flexible helix-forming ligand with a (1*R*,2*R*)-cyclohexyl backbone and benz[*a*]-anthracene-based sidearms.

The condensation of (1*R*,2*R*)-diaminocyclohexane, (*R*,*R*)-**1**, and 1-hydroxybenz[*a*]anthracene-2-carboxaldehyde, **2**, in ethanol gives the salen ligand (*R*,*R*)-**3** (Scheme 1).[4] Tautomerizations are well known for Schiff bases,[5] and both

Scheme 1. Synthesis of (*R*,*R*)-**3** and Its Zn^{II} and Fe^{II} Complexes
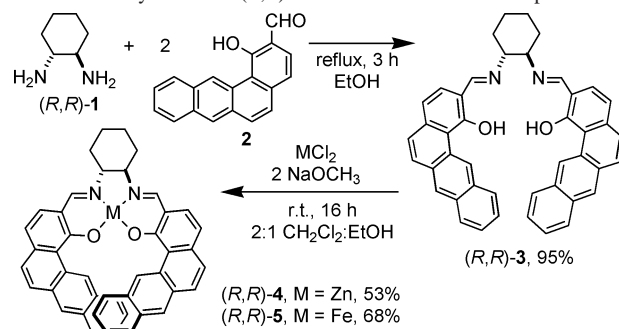
keto-amine and enol-imine forms are observed by electronic spectroscopy, while averaged signals are seen by NMR due to fast exchange. Reaction of (*R*,*R*)-**3** with sodium methoxide and MCl$_2$ (M = Zn, Fe) gives the M^{II} complexes (*R*,*R*)-**4** and (*R*,*R*)-**5**.[6] The Zn^{II} complex is diamagnetic and has well-resolved ^{1}H and ^{13}C NMR solution spectra while the Fe^{II} complex is paramagnetic (m_{eff} = 5.14, 4 unpaired electrons) and the ^{1}H NMR spectrum has broad signals from −24.1 to +41.7 ppm.

Single crystals of [(*R*,*R*)-**4**(pyridine)]·[0.5C$_5$H$_5$N C$_2$H$_5$OH] were grown by diffusion of diethyl ether into a pyridine solution of (*R*,*R*)-**4**.[7] The structure (Figure 1) reveals a distorted square pyramidal geometry at zinc, with an axial

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(1) For examples see: (a) Zhu, Y.-Z.; Li, Z.-P.; Ma, J.-A.; Tang, F.-Y.; Kang, L.; Zhou, Q.-L.; Chan, A. S. C. *Tetrahedron: Asymmetry* **2002**, *13*, 161. (b) Maruoka, K.; Murase, N.; Yamamoto, H. *J. Org. Chem.* **1993**, *58*, 2938. (c) End, N.; Pfaltz, A. *Chem. Commun.* **1998**, 589. (d) End, N.; Macko, L.; Margareta, Z.; Pfaltz, A. *Chem. Eur. J.* **1998**, *4*, 818. (e) Guo, C.; Qui, J.; Zhang, X.; Verdugo, D.; Larter, M. L.; Christie, R.; Kenney, P.; Walsh, P. J. *Tetrahedron* **1997**, *53*, 4145. (f) Seitz, M.; Kaiser, A.; Stempfhuber, S.; Zabel, M.; Reiser, O. *Inorg. Chem.* **2005**, *44*, 4630.

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(3) Wiznycia, A. V.; Desper, J.; Levy, C. J. *Chem. Commun.* **2005**, 4693.

(4) A mixture of (*R*,*R*)-**1** (0.421 g, 7.4 mmol) and **2** (2.006 g, 3.7 mmol) in ethanol (150 mL) was refluxed for 3 h. The resulting suspension was filtered while hot, and the yellow solid was washed with 50 mL of boiling ethanol and dried in vacuo to give (*R*,*R*)-**3** (2.177 g, 95%). Anal. Calcd for C$_{44}$H$_{34}$N$_2$O$_2$: C 84.86, H 5.50, N 4.50. Found: C 84.52, H 5.67, N 4.48.

(5) (a) Herzfeld, R.; Nagy, P. *Spectrosc. Lett.* **1999**,*32*, 57. (b) Császár, J. *Acta Phys. Chem.* **1979**, *25*, 129. (c) Charette, J.; Faltlhansl, G.; Teyssie, Ph. *Spectrochim. Acta* **1964**, *20*, 597.

(6) Anhydrous zinc chloride (0.066 g, 0.48 mmol), sodium methoxide (0.078 g, 1.5 mmol), and (*R*,*R*)-**3** (0.301 g, 0.48 mmol) were suspended into a 2:1 mixture of methylene chloride/ethanol (15 mL) and stirred for 16 h. The reaction mixture was concentrated and filtered to give a yellow solid that was subsequently dissolved into THF (20 mL) and filtered to remove fine insoluble solids. The clear filtrate was stirred for 2 h, resulting in the formation of a yellow precipitate, which was collected and washed consecutively with THF (5 mL) and ethanol (5 mL) to afford (*R*,*R*)-**4** (0.177 g, 53% yield). Anal. Calcd for C$_{44}$H$_{32}$N$_2$O$_2$Zn: C 77.02, H 4.70, N 4.08. Found: C 77.19, H 4.65, N 4.21. (*R*,*R*)-**5** was synthesized in 68% yield by the same general procedure, with some variation in workup (see Supporting Information). Anal. Calcd for C$_{44}$H$_{32}$N$_2$O$_2$Fe: C 78.11, H 4.77, N 4.14. Found: C 78.12, H 5.02, N 3.90.

(7) The sample used for crystallization was not thoroughly dried of residual solvent, and this is the source of ethanol in the crystals. Crystal data for (*R*,*R*)-**4**(pyridine)·[0.5C$_5$H$_5$N C$_2$H$_5$OH]: Bruker SMART 1000, yellow prisms, 0.44 × 0.24 × 0.22 mm^3, C$_{53.5}$H$_{44.5}$N$_{3.5}$O$_3$Zn, M = 849.80, hexagonal, a = 26.3597(6) Å, c = 10.2518(5) Å, V = 6169.0-(4) Å^3, T = 100(2) K, space group $P6_5$, Z = 6, 2θ collection range 0.89−30.10°, h ± 37, k ± 36, l ± 14, μ(Mo Kα) = 0.649 mm^{-1}, graphite monochromater, 71 849 reflections collected, 12 068 unique (R_{int} = 0.0304) which were used in all calculations. R1 = 0.0395 (all data) and wR2(F^2) = 0.0996. Flack parameter = −0.003(6).
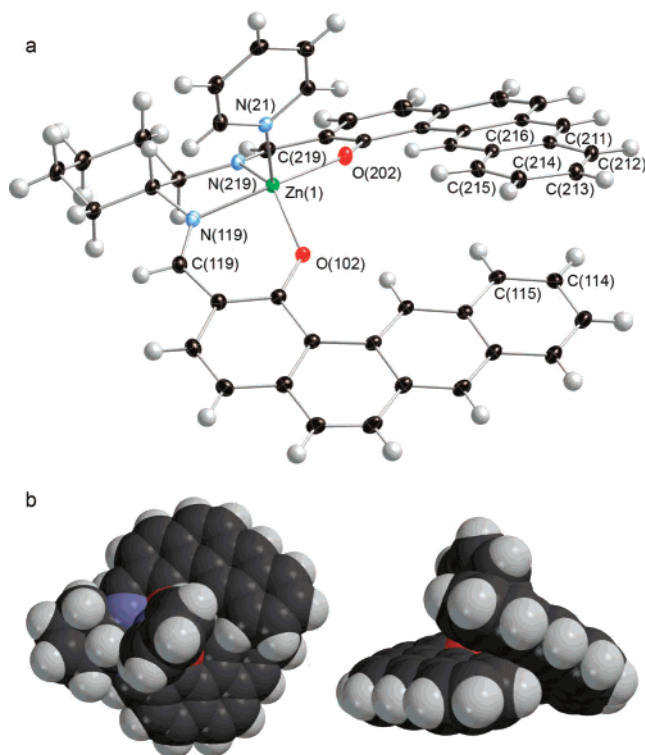
Figure 1. (a) Thermal ellipsoid plot (50%) of [(R,R)-**4**(py)]. Selected bond lengths (Å): Zn–N(119) 2.0631(16), Zn–N(219) 2.1046(15), Zn–O(102) 1.9784(13), Zn–O(202) 1.9839(13), Zn–N(21) 2.1233(16), C(119)–N(119) 1.278(2), C(219)–N(219) 1.283(2). Centroid C(211)–C(216) is 3.665 Å from C(114) and 3.656 Å from C(115) (b) Space-filling models of [(R,R)-**4**(py)]: two views.

pyridine ligand. The complex has exclusively *M* helicity, consistent with that seen by Fabbrizzi et al. for a *bis*-imine *bis*-quinoline Cu[I] complex with the same (R,R)-cyclohexyl backbone.[8] The benz[*a*]anthryl sidearms are significantly overlapped, but the large 40.1° angle between them and the relatively large spacing indicate that little face-to-face $\pi-\pi$ interaction is present.

The structure of (R,R)-**5**(py)[9] is profoundly different from that of the zinc complex, since it has a 1:1 mixture of *M* and *P* comformers (Figure 2). The angles between the sidearm planes are very similar for the two molecules (*M*, 24.2°; *P*, 21.8°) and significantly closed down compared to (R,R)-**4**(py). The relatively small angle and the half-ring offset face-to-face stacking of the sidearms suggest that $\pi-\pi$ interactions are present in each conformer. Indeed, centroid-to-carbon distances are well within the 3.4–3.6 Å range expected for attractive $\pi-\pi$ stacking:[10] [C(111)–C(116)] to C(214) and [C(311)–C(316)] to C(414) are 3.46 and 3.47

(8) Amendola, V.; Fabbrizzi, L.; Linati, L.; Mangano, C.; Pallavicini, P.; Pedrazzini, V.; Zema, M. *Chem. Eur. J.* **1999**, *5*, 3679. Racemic ligand was used; (R,R) gives *M* helices and (S,S) gives *P* helices.

(9) Single crystals suitable for X-ray analysis were grown by diffusion of ethanol into a pyridine solution of (R,R)-**5**. Crystal data for (R,R)-**5**(pyridine): Bruker SMART 1000, black prisms, 0.33 × 0.18 × 0.09 mm³, C₄₉H₃₇N₃O₂Fe, M = 755.67, monoclinic, a = 10.7342(11) Å, b = 19.595(2) Å, c = 17.7357(19) Å, b = 105.904(2)°, V = 3587.8(7) Å³, T = 100(2) K, space group P2₁, Z = 4, 2θ collection range 2.01–30.03°, h ± 15, k ± 27, l ± 24, μ(Mo Kα) = 0.468 mm⁻¹, graphite monochrometer, 41 757 reflections collected, 20 505 unique (Rᵢₙₜ = 0.0322) which were used in all calculations. R1 = 0.0539 (all data) and wR2(F²) = 0.1107. Flack parameter = 0.002(9).
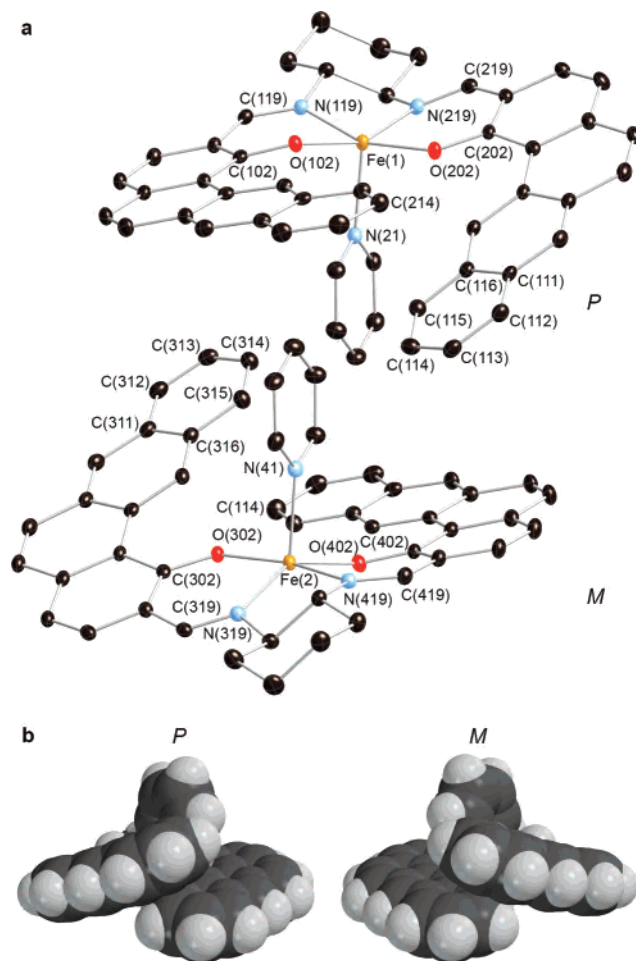
Figure 2. (a) Thermal ellipsoid plot (50%) of the two conformers, showing their relative orientation in the crystal of (R,R)-**5**(py). Selected bond lengths (Å): Fe(1)–N(119) 1.489(3), Fe(1)–N(219) 2.1132(19), Fe(1)–O(102) 1.9704(17), Fe(1)–O(202) 19817(17), Fe(1)–N(21) 2.147(2), C(119)–N(119) 1.295(3), C(219)–N(219) 1.288(3), Fe(2)–N(319) 2.0631(16), Fe(2)–N(419) 2.1046(15), Fe(2)–O(302) 1.9930(16), Fe(2)–O(402) 1.9642-(17), Fe(2)–N(41) 2.154(3), C(319)–N(319) 1.294(3), C(419)–N(419) 1.284(3). (b) Space filling models of the two conformers.

Å, respectively. Since the $\pi-\pi$ interactions appear nearly identical for the two conformers, they do not result any significant thermodynamic preference for one over the other. A comparison of the two space-filling models of (R,R)-**5**(py) (Figure 2b) reveals that they are nearly enantiomeric and that the main difference is the relative positions of the benz-[*a*]anthryl sidearms. The cyclohexyl backbone has a very similar diequatorial conformation for the *M* and *P* forms.

The 1:1 mixture of helical conformers seen for [(R,R)-**5**(py)] in the solid state is somewhat surprising given that the two forms are diastereomeric and that the overlap of the sidearms would seem to make interconversion unfavorable. DFT calculations on minimized structures consistently predict that the *M* form is favored for both Zn[II] and Fe[II] complexes.[11] The difference is generally in the 1–4 kcal/mol range, except in the case of (R,R)-**5**(py), where it is only 0.1 kcal/mol. This small energy difference combined with the general preference of chiral compounds to crystallize as racemates

(10) (a) Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*; Wiley: New York, 2000; p 26. (b) Hunter, C. A.; Sanders, K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525.

results in the adoption of pseudo-racemic conformers in the solid state[12] for the iron(II) complex when pyridine is coordinated. This is an unusual occurrence and has only been seen for few metal complexes[13,14] and even fewer mononuclear complexes.[14]

In order to analyze the solution constitution and behavior of the metal complexes, we turned to NMR and ECD spectroscopies. The ^{1}H NMR spectrum of (R,R)-**4** is sharp and is consistent with a single C_2-symmetric compound. The spectrum does not change appreciably over a wide temperature range ($-90-110$ °C), and no exchange processes are evident. The same results are found when (R,R)-**4**(py) was dissolved for the studies, indicating that the pyridine does not appreciably affect the identity of the complexes in solution or their solution behavior. Parallel NMR studies of the paramagnetic Fe(II) complexes were precluded due to the broadness of the spectra.

The electronic and ECD spectra of (R,R)-**4** and (R,R)-**5** (Figure 3) are similar in appearance, with the iron complex having broader signals and additional ligand field transitions. The low-energy envelope (350−460 nm) is attributable primarily to the $\pi-\pi^*$ transition of the imine groups.[15] This transition gives a negative Cotton effect at long wavelengths, confirming a diequatorial 1R,2R configuration and noncoplanar imines.[15] The benz[a]anthryl chromophore absorbs in the 200−380 nm region, with the strongest absorption from 200 to 300 nm.[16] The ECD spectra show strong signals, suggesting that there is one dominant helical form in solution, as opposed to a 1:1 M/P mixture. This conclusion is supported by DFT simulated spectra which show a good match between the experimental spectrum of (R,R)-**4** and the simulated spectrum of the M conformer. Correspondingly, the simulated P spectrum resembles the mirror image of both the experimental spectrum and the simulated M conformer spectrum. The ECD spectra of freshly prepared solutions (R,R)-**4**(py) and (R,R)-**5**(py) show no significant differences to those of (R,R)-**4** and (R,R)-**5**, respectively. This result indicates that the same structure and conformer distribution is obtained whether pyridine is initially coordinated or not.
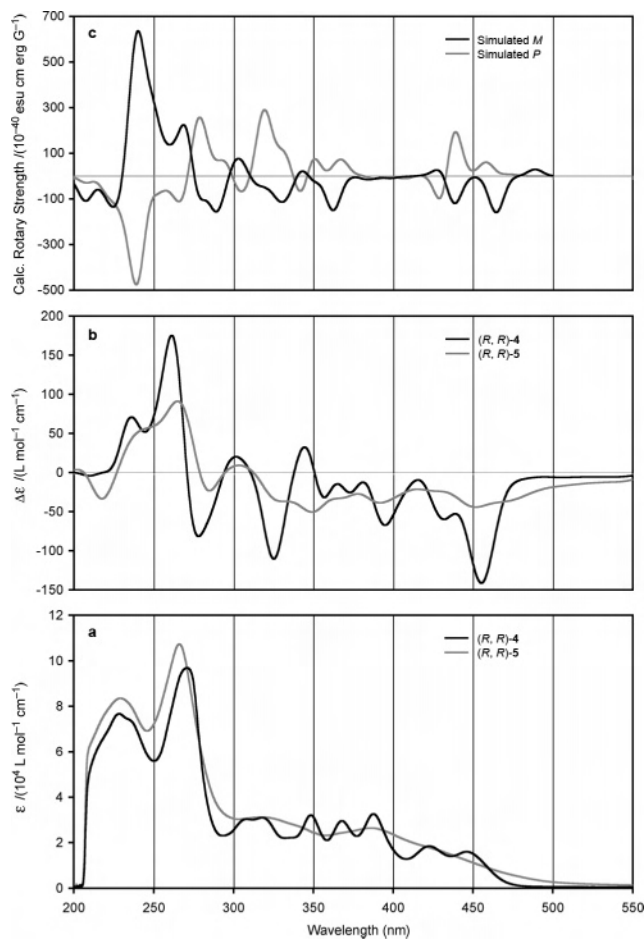
(11) B3LYP* calculations carried out using ADF showed the M conformer to be more favorable as follows (kcal/mol). (R,R)-**4**, 1.1; (R,R)-**4**(py), 3.6; (R,R)-**5**, 1.9; (R,R)-**5**(py), 0.1.
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(16) Jones, R. N. J. Am. Chem. Soc. **1945**, 67, 2127.

Figure 3. (a) UV−visible spectra in THF. (b) ECD spectra in THF. (c) Simulated ECD spectra for the M and P conformers of (R,R)-**4**. The concentrations of (R,R)-**4** and (R,R)-**5** are 2.5×10^{-5} and 1.5×10^{-5} M, respectively, for the experimental spectra.

In summary, we have developed a monohelix-forming salen ligand that produces complexes with varying degrees of attractive $\pi-\pi$ stacking for the overlapped benz[a]anthryl sidearms. In THF the M conformer predominates for both the Zn^{II} and Fe^{II} complexes. The Zn^{II} complex maintains this structure in the solid state, but the Fe^{II} complex crystallizes as a 1:1 mixture of diastereomeric helices from pyridine. Thus, for (R,R)-**5** we have a rare example[12,13] of a compound that can have one dominant helicity in solution (M) but can form a pseudo-racemic 1:1 M/P mixture upon crystallization. The necessity of the coordinated pyridine for this conversion is as yet uncertain since we have not been able to obtain structures of crystals grown from other solvents. These results suggest that complexes of this ligand could be the basis for chiroptical switches. Further investigation of the metal complexes of (R,R)-**3** and their potential as asymmetric catalysts is currently underway.

Supporting Information Available: Detailed experimental procedures, spectral data, and crystallographic information. This material is available free of charge via the Internet at http://pubs.acs.org.

IC061553Z