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Article

Double-Stranded Monohelical Complexes from an Unsymmetrical Chiral Schiff-Base Ligand

Azadeh Lalehzari, John Desper, and Christopher J. Levy*

Department of Chemistry, Kansas State University, 111 Willard Hall, Manhattan, Kansas 66506

A new Schiff-base ligand is prepared by a two-step reaction of 3-formylsalicylic acid and (1R, 2R)-diaminocyclohexane in alcoholic solvents. The 1:1 condensation product exists as a zwitterion in the solid state and forms pleated hydrogen-bonded sheets. Metalation of the ligand with divalent iron, nickel, cobalt, and zinc resulted in the formation of double-stranded monohelices with exclusively M-helicity. Each complex has two tridentate ligands, with the carboxylic acid groups remaining uncoordinated. In the crystal lattice, these complexes form extended M-helical strands through intermolecular hydrogen bonding interactions. Metalation of the ligand with copper salts resulted in a distinctly different type of complex, in which the ligand has transformed into a symmetric tetradentate salen ligand with uncoordinated carboxylic acid groups.

Introduction

Well-defined chiral metal complexes and metal-containing helical species are of great interest because of their similarities to bioinorganic molecules as well as their uses in asymmetric catalysis and supermolecular chemistry.[1,2] However, there are still significant challenges in the prediction of complexation and the disposition of metal binding sites.[3] This is particularly true in the predetermination of chirality in octahedral complexes with tridentate ligands.[4] It is common for homoleptic complexes of tridentate ligands to be di- or polynuclear, and even when mononuclear complexes are obtained there is the possibility of two or more stereoisomers. Looking at the most general mononuclear case, two linear ABC-type ligands can coordinate to a metal center in either a facial (**A**, Chart 1) or meridional (**B**, Chart 1) fashion. The facial mode has 11 possible stereoisomers, whereas the meridional mode has two, the minus (M) and plus (P) helical forms (alternately Λ and Δ, respectively). Thus, stereochemical control is more easily achieved for

Chart 1. Octahedral Complexes with Two Tridentate ABC-Type Ligands (**A**, **B**) and Structure of the Chiral 3-Formylsalicylic Acid Derived Schiff-Base Ligands Used in This Work (**C**, Donors in Blue)
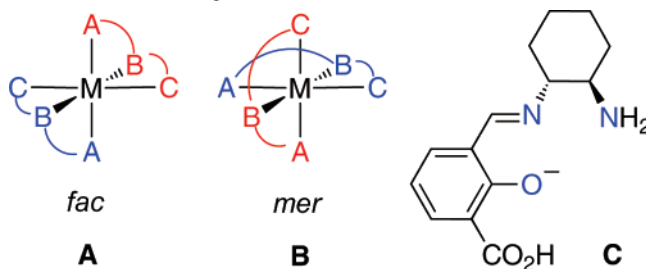

meridional complexes. For a chiral nonracemic ligand, the M and P forms are diastereomeric, and it is possible to obtain a single chiral isomer upon coordination. Selectivity of this type has not been widely demonstrated, and even for common chiral Schiff-base ligands only a few examples of this complexation mode have been reported.[5–9]

In this contribution, the coordination of a new chiral Schiff-base ligand derived from 3-formylsalicylic acid

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* To whom correspondence should be addressed. E-mail: clevy@ksu.edu.

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Chart 2. General Structures of Complexes of Unsymmetrical 3-FSA Derived Ligands

M = bivalent metal ion
R = alkyl, aryl group
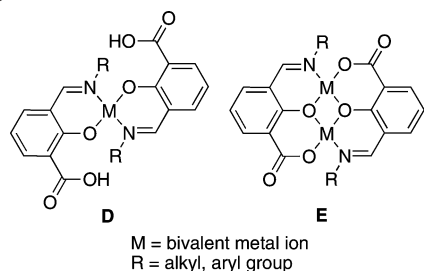
(3-FSA) is examined (**C**, Chart 1). Generally, 3-FSA-based Schiff-base ligands do not provide a carboxylate donor when coordinated to a single metal (**D**, Chart 2),[10] although dinuclear complexes usually do involve carboxylate coordination (**E**, Chart 2).[10–16] In the current study, the ligand has been modified to include an additional donor (primary amine), resulting in a tridentate ligand that can form octahedral ML$_2$ complexes. In this design, the carboxylic acid groups remain uncoordinated and available for intermolecular hydrogen bonding or further chemical modifications. No chiral ligands with this design have been reported to date, and of the few achiral examples that exist,[10–16] mononuclear ML$_2$ complexes are proposed in only one case.[10b] In this article, we describe the successful application of this approach and demonstrate general control of the chiral environment in meridional octahedral complexes of the type ML$_2$, for a variety of first-transition series metal ions. The carboxylic acid functionalities do indeed provide for extended hydrogen-bonding networks in the solid state.

Experimental Section

All of the reactions were carried under inert atmospheres. Solvents used in complexation reactions were dried and degassed prior to vacuum transfer into reaction vessels. Methanol was dried over magnesium and triethylamine was dried over calcium hydride. ACS reagent grade methanol was used without further purification for ligand syntheses. NMR solvents were dried over 4 Å molecular sieves. Complexation reactions were carried out using diffusion crystallization techniques in 7 mm OD borosilicate tubing. 3-FSA

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was prepared according to the methods of Duff and Bills.[17] (1R,2R)-diaminocyclohexane (DAC) was resolved according to literature procedures.[18] ^{1}H and ^{13}C NMR were obtained on a Varian Unity 400 MHz spectrometer employing residual solvent protons as an internal standard. Crystallographic data was collected using either a Bruker SMART 1000 CCD, a Bruker-AXE SMART APEX CCD, or a κAPEX 2II diffractometer. Electrospray Ionization spectra were acquired on an LCT Premier (Waters Corp., Milford MA) time-of-flight mass spectrometer. The instrument was operated at 10 000 resolution (W mode) with dynamic range enhancement that attenuates large intensity signals. Optical rotations were measured using a PerkinElmer 241 polarimeter. Electronic spectra were acquired on a Hewlett-Packard 8453 spectrometer, using a 1.00 cm path length quartz cell.

3,3′-[(1R,2R)-1,2-Cyclohexanediylbis(nitrilomethylidyne)]bis-[2-hydroxybenzoic Acid], (R,R)-1. A solution of 3-formylsalicylic acid (1.55 g, 9.33 mmol) and (1R,2R)-diaminocyclohexane (0.53 g, 4.67 mmol) in methanol (15 mL) was heated to reflux for 4 h under argon. The resulting yellow precipitate was collected by filtration to give (R,R)-**1** (1.845 g, 96% yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 1.40 (m, 2H), 1.83 (m, 4H), 2.18 (d, 2H), 4.26 (d, 2H), 6.66 (t, 2H), 7.64 (d, 2H), 8.03 (d, 2H), 8.76 (s, 2H, H−N═), 13.11 (br), 15.98 (br). ^{13}C NMR (CDCl$_3$, 50 MHz): δ 19.22, 24.16, 33.51, 114.96, 115.81, 119.89, 141.06, 141.75, 168.07, 169.98, 176.69. [α]$^D_{25}$ = −8.50° in ethanol. MS (*m/z*): [M + Na]$^+$ Calcd for C$_{22}$H$_{22}$N$_2$O$_6$·Na$^+$, 433.1375; found, 433.1389 (3.2 ppm).

3-(((1R,2R)-2-Aminocyclohexylimino)methyl)-2-hydroxybenzoic Acid, (R,R)-2. A solution of (R,R)-**1** (1.65 g, 4.03 mmol) and (1R, 2R)-diaminocyclohexane (0.46 g, 4.03 mmol) in methanol (20 mL) was heated to 40−50 °C for 4 h under argon. The resulting white precipitate was collected by filtration to give (R,R)-**2** (1.93 g, 91% yield). [α]$^D_{25}$ = −3.04° in ethanol. UV−vis (nm, pyridine); 261, 341, 368. ^{1}H NMR of **2a** (DMSO-d_6, 400 MHz): δ 1.32−2.05 (m, 8H), 3.16 (m, 2 H), 6.58 (t, 1H), 7.2 (bs, ∼ 3H), 7.75 (d, 1H), 7.82 (d, 2H), 8.75 (s, 1H), 18.02 (br), ^{1}H NMR of **2b** (DMSO-d_6, 400 MHz): δ 1.15−1.95 (m, 8H), 3.1−3.2 (m, 2 H), 4.1 (bs, ∼2 H), 6.50 (t, 1H), 7.61 (d, 1H), 7.71 (d, 1H), 8.61 (s, 1H). ^{13}C NMR (DMSO-d_6, 50 MHz): δ 22.96, 28.46, 31.88, 32.31, 53.57, 70.44, 113.76, 120.08, 121.55, 128.71, 132.28, 158.18, 164.62, 170.00 MS (*m/z*): [M + Na]$^+$ Calcd for C$_{14}$H$_{18}$N$_2$O$_3$·Na$^+$, 285.1215; found, 285.1224 (3.2 ppm).

General Metalation Procedure. The following procedure was carried out in a glove box with a nitrogen atmosphere. Methanol (1 mL) was added to an excess amount of metal salt (∼15 equiv). After 10 min of vigorous shaking, the solution/suspension was filtered and any residual metal salt was dried and weighed to determine the amount dissolved. (R,R)-**2** was separately added to methanol (1 mL). Dry triethylamine was added dropwise to (R,R)-**2** until a clear solution was obtained (∼0.1 mL added). The solution was filtered to eliminate any particles. The solution containing (R,R)-**2** was layered on top of the solution of metal salt, and the tube was sealed. Crystals were usually obtained after 1−3 days at ambient temperature. The crystals were isolated and washed with cold methanol (5 × 1 mL), and the product was dried in vacuo. Yields ranged from 56 to 86% based on the amount of ligand used.
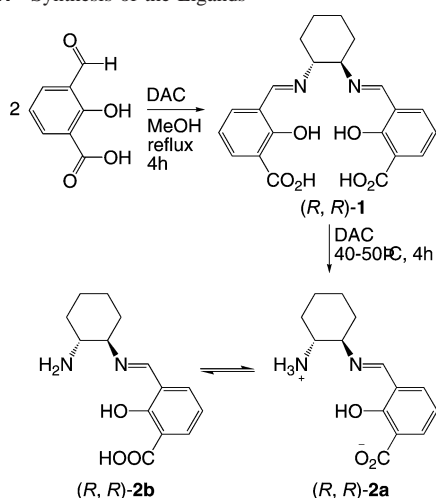
4. Anhydrous FeCl$_2$ (0.1204 g 0.949 mmol) and (R,R)-**2** (0.0315 g 0.120 mmol) were combined following the general procedure. After 3 days, 0.020 g (0.035 mmol, 58% yield) of red crystals were obtained. MS (*m/z*): [M + H]$^+$ Calcd for C$_{28}$H$_{34}$N$_4$O$_6$Fe·H$^+$, 579.1906; found, 579.3683.

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Scheme 1. Synthesis of the Ligands

Scheme 2. Synthesis of Metal Complexes by Solvent Diffusion

4, M = Fe, 58%;
5, M = Co, 84%;
6, M = Ni, 68%;
7, M = Zn, 84%

R = CO$_2$H for all complexes

8, 86% from Cu(OTf)$_2$
80% from Cu(OTf)

5. Method A. Anhydrous Ni(OTf)$_2$ was used as the metal salt. After 48 h, 0.036 g (0.062 mmol, 84% yield) of yellow crystals were obtained from 0.038 g (0.145 mmol) of (*R,R*)-**2** and 0.058 g (0.161 mmol) of Ni(OTf)$_2$.

Method B. Anhydrous NiI$_2$ was used as the metal salt. After 48 h, 0.042 g (0.072 mmol, 73% yield) of yellow crystals were obtained from 0.052 g (0.198 mmol) of (*R,R*)-**2** and 0.099 g (0.318 mmol) of NiI$_2$. MS (*m/z*): [M + H]$^+$ Calcd for C$_{28}$H$_{34}$N$_4$O$_6$Ni·H$^+$, 581.1910; found, 581.1893 (2.9 ppm).

6. Anhydrous CoI$_2$ was used as the metal salt. After 24 h, 0.025 g (0.043 mmol, 68% yield) of pink crystals were obtained from 0.034 g (0.128 mmol) of (*R,R*)-**2** and 0.077 g (0.247 mmol) of CoI$_2$. MS (*m/z*): [M + Na]$^+$ Calcd for C$_{28}$H$_{32}$N$_4$O$_6$Co·Na$^+$, 603.1630; found, 603.1624 (1.0 ppm).

7. Anhydrous ZnCl$_2$ was used as the metal salt. After 48 h, 0.038 g (0.065mmol, 84% yield) of yellow crystals were obtained from 0.040 g (0.152 mmol) of (*R,R*)-**2** and 0.150 g (1.100 mmol) of ZnCl$_2$. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 1.05−2.18 (m, 14 H), 3.16−4.34 (m, 10H), 6.79 (t, 1H), 7.62 (d, 1H), 8.03 (d, 1H), 8.45 (s, 1H). ^{13}C NMR (DMSO-d_6, 50 MHz): δ 24.05, 27.64, 33.85, 48.62, 55.53, 63.79, 115.46, 121.47, 122.59, 124.33, 139.78, 165.48, 170.00, (the C=N carbon is broadened due to the quadropolar effect of ^{15}N) MS (*m/z*): [M + H]$^+$ Calcd for C$_{28}$H$_{34}$N$_4$O$_6$Zn·H$^+$, 587.1848; found, 587.1864 (2.7 ppm).

8. Method A. Anhydrous Cu(OTf)$_2$ was used as the metal salt. After 24 h, 0.039 g (0.077 mmol, 86% yield) of maroon crystals were obtained from 0.047 g (0.179 mmol) of (*R R*)-**2** and 0.078 g (0.217 mmol) of Cu(OTf)$_2$.

Method B. Anhydrous Cu(OTf)·C$_6$H$_5$CH$_3$ was used as the metal salt. After 24 h, 0.032 g (0.063 mmol) of maroon crystals were obtained from 0.041 g (0.157 mmol) of (*R,R*)-**2** and 0.043 g (0.083 mmol) of copper(I) trifluoromethanesulfonate toluene adduct, (CF$_3$SO$_3$)Cu·C$_6$H$_5$CH$_3$, 80% yield. ^{1}H and ^{13}C NMR spectra for this paramagnetic compound were unresolved. MS (*m/z*): [M + H]$^+$ Calcd for C$_{22}$H$_{20}$N$_2$O$_6$Cu·H$^+$, 472.0696; found, 472.0717 (4.4 ppm).

Results and Discussion

Ligand Synthesis. Ligand (*R,R*)-**2**, was prepared by a two step condensation reaction of 3-FSA with (1*R*,2*R*)-diaminocyclohexane (Scheme 1). In the first step, 3-FSA is added in a 2:1 ratio to the diamine to give the symmetric Schiff-base product, (*R,R*)-**1**. This compound has been previously
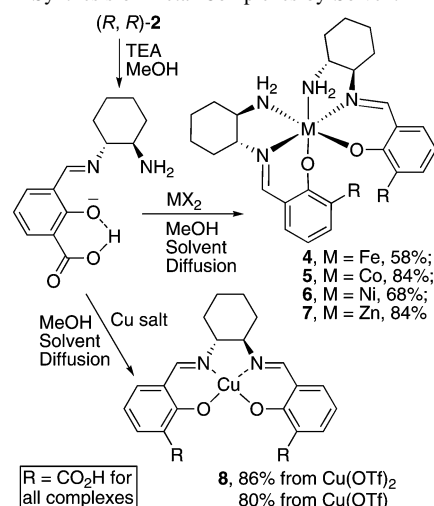
reported,[19] but synthetic details and characterization were not provided. The addition of an equimolar amount of DAC to (*R,R*)-**1** yields the unsymmetric ligand (*R,R*)-**2** as a white solid. The use of an alcoholic solvent, in this case methanol, and control of the temperature in the 40−50 °C range are crucial for the formation and isolation of this product. The highest yield is achieved when the reaction is done at high concentrations with reaction times under 6 h. The starting material (*R,R*)-**1** is soluble in warm methanol, whereas the product (*R,R*)-**2** requires boiling methanol to fully dissolve. A one-pot synthesis of (*R,R*)-**2** from 3-formyl-salicylic acid and the diamine is possible but delivers a lower yield and product mixtures. Given the high yield of the two-step process and the necessity for tight control of the reaction conditions in the second step, the former is preferable. Solutions of (*R,R*)-**2** show modest sensitivity to moisture and should therefore be handled in a dry atmosphere.

The 21 °C ^{1}H NMR spectrum of (*R,R*)-**2** in DMSO-d_6 shows the presence of two sets of peaks; a major and a minor with a ratio of 1:6.7 (15% minor). Both sets show peaks assignable to N=CH, phenol, and cyclohexyl protons at 8.75 (8.61), 6.58−7.82 (6.50−7.71), and 1.32−3.16 (1.15−3.2) ppm, respectively (data in parenthesis indicates the shifts for the minor set). In the major set, the phenol proton (hydrogen-bonded) appears as a broad singlet at 18.02 ppm, and the ammonium protons appear as a broad singlet at 7.2 ppm. The minor set of signals shows only one broadened signal, a singlet at 4.1 ppm, which is consistent with the NH$_2$ group of a primary amine. This data suggests that (*R,R*)-**2** exists in solution as both the zwitterion (*R,R*)-**2a** and the neutral amine (*R,R*)-**2b** forms (Scheme 1). An equilibrium is confirmed by VT-NMR: the distribution changes to 35% (*R,R*)-**2b** upon warming to 70 °C and reverts back to the initial composition upon cooling to 21 °C.

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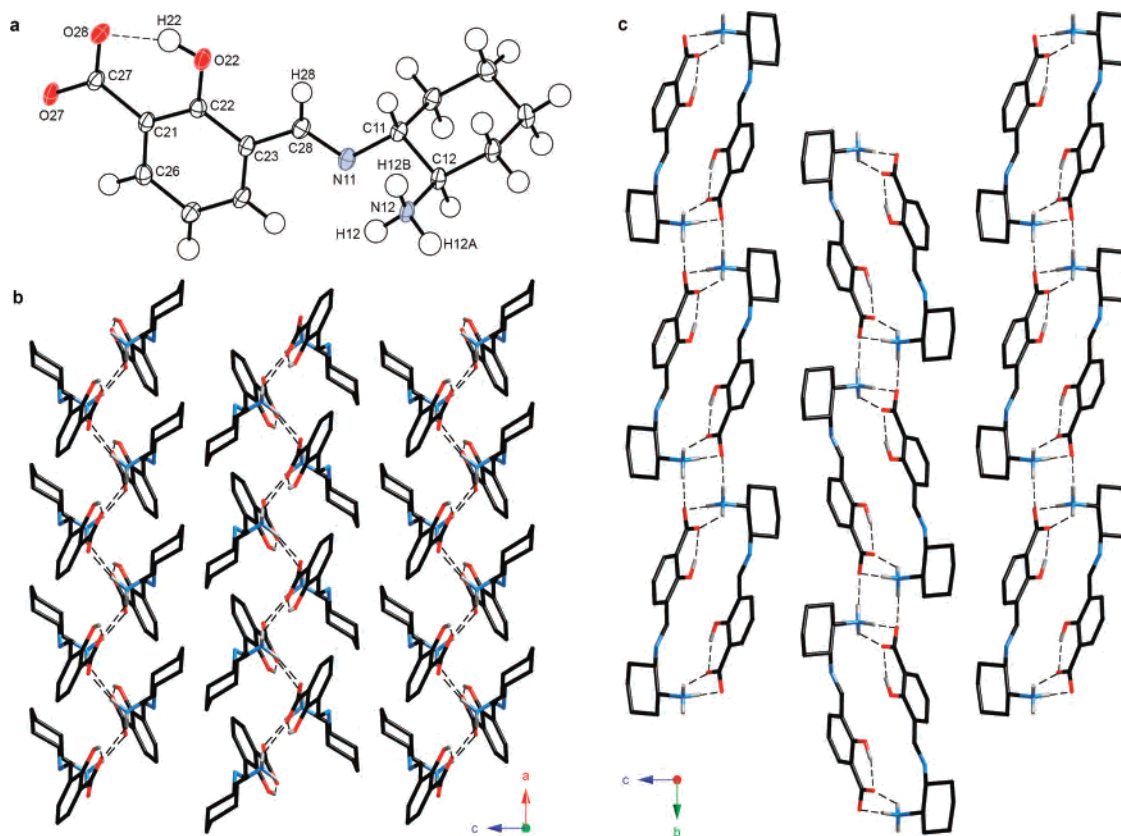
Figure 1. Crystal structure of ligand (*R,R*)-**2**. (a) Thermal ellipsoid plot (50%). (b) Packing diagram along the *b* crystallographic axis. (c) Packing diagram along the *a* crystallographic axis.

Table 1. Crystal Data for (*R,R*)-**2** and Metal Complexes **3**−**8**

compound	(*R,R*)-**2**	**4**	**5**	**6**	**7**	**8**
formula	$C_{28}H_{36}N_4O_6$	$C_{28}H_{34}FeN_4O_6$	$C_{28}H_{34}CoN_4O_6$	$C_{28}H_{34}NiN_4O_6$	$C_{28}H_{34}ZnN_4O_6$	$C_{23}H_{24}CuN_2O_7$
M	524.61	578.44	581.52	581.30	587.96	503.98
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
color	yellow	red	pink	green-brown	yellow	maroon
a (Å)	6.1675(8)	8.8032(4)	8.8100(8)	8.8514(6)	8.7802(7)	7.5321(7)
b (Å)	11.9167(15)	12.5533(6)	12.4866(12)	12.5256(9)	12.5067(10)	16.0522(14)
c (Å)	18.033(2)	12.3334(6)	12.3007(12)	12.1886(9)	12.3400(10)	17.4225(15)
α (deg)	90	90	90	90	90	90
β (deg)	90	95.159(2)	94.572(4)	94.5630(10)	94.8560(10)	92.7830(10)
γ (deg)	90	90	90	90	90	90
V (Å^3)	1325.3(3)	1357.43(11)	1348.9(2)	1347.06(10)	1350.21(19)	2104.0(3)
space group	$P2_12_12_1$	$P2_1$	$P2_1$	$P2_1$	$P2_1$	$P2_1$
Z	2	2	2	2	2	4
T (K)	100(2)	100(2)	173(2)	100(2)	100(2)	100(2)
μ (mm^{-1})	0.093	0.605	0.686	0.770	0.959	1.089
N	10 527	50 859	9993	11 861	15 953	18 451
N_{ind}	1867	12 859	5362	6077	6375	9615
R_{int}	0.0521	0.0255	0.0516	0.0254	0.0256	0.0238
R1^a	0.0479	0.0246	0.0465	0.0345	0.0298	0.0335
wR2^a	0.1163	0.0648	0.1087	0.0818	0.0707	0.0807
R1 (all data)	0.0567	0.0264	0.0612	0.0383	0.0319	0.0405
wR2 (all data)	0.1214	0.0657	0.1193	0.0835	0.0718	0.0844
GOF	1.095	1.028	0.973	1.056	1.026	0.973
flack parameter	1.4(16)	0.012(4)	0.001(16)	0.001(10)	0.008(7)	0.009(9)

^{a} R1 $= \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $F_o > 2\sigma(F_o)$ and wR2 $= \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_c^2)]\}^{1/2}$.

Metal Complex Synthesis. Complexations were carried out by solvent diffusion of the depronated ligand into a solution of the metal salts. In methanol, crystallization stops after 1−3 days, giving yields of 56−86%. The ligand anion is generated in situ by suspending (*R,R*)-**2** in methanol and

adding triethylamine until a clear solution is obtained. The reaction does not occur in the absence of added base, as the neutral ligand is unreactive toward the metal salts examined. Exact stoichiometry in the base addition is not necessary because triethylamine only carries out a single deprotonation,

Table 2. Selected Bond Lengths (Angstroms), Angles (Degrees), and Dihedral Angles (Degrees) for (*R,R*)-**2**

C(11)−N(11)	1.459(3)	N(11)−C(11)−C(12)	110.53(19)
C(12)−N(12)	1.496(3)	C(11)−C(12)−N(12)	110.08(16)
C(28)−N(11)	1.270(3)	C(11)−N(11)−C(28)	115.4(2)
C(22)−O(22)	1.338(3)	N(11)−C(28)−C(23)	122.3(2)
C(21)−C(27)	1.501(3)	O(27)−C(27)−O(28)	123.7(2)
C(27)−O(27)	1.268(3)	C(11)−N(11)−C(28)−C(23)	172.35(18)
C(27)−O(28)	1.265(3)	C(22)−C(21)−C(27)−O(27)	178.42(18)

Table 3. Hydrogen Bonding Distances (Angstroms) and Angles (Degrees) in (*R,R*)-**2**

entry	D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	DHA (°)
1	O(22)−H(22)···O(28)	0.88(3)	1.73(3)	2.540(2)	152(3)
2	N(12)−H(12′)···O(27) (B)	0.93(3)	1.79(3)	2.719(2)	176(3)
3	N(12)−H(12″)···O(27) (B)	1.01(3)	1.80(3)	2.793(3)	169(2)
4	N(12)−H(12‴)···O(28) (C)	0.90(3)	2.17(3)	2.942(3)	144(2)

nominally to form a phenoxide. Tautomerization to give a neutral amine and an intramolecularly hydrogen-bonded proton is likely.

Reactions of the anhydrous salts $FeCl_2$, CoI_2, NiX_2 (X = I, OTf) and $ZnCl_2$ result in the formation of **4**−**7**, respectively (Scheme 2). All of the complexes are enantiomerically pure, with each ligand having the *R,R* configuration. These compounds are 2:1 ligand to metal complexes, and each has approximately octahedral geometry and a double-stranded helical structure. Crystalline products are also isolated from reactions with copper salts, but these have a distinctly different composition: the metal center is coordinated by the doubly deprotonated form of the tetradentate ligand (*R,R*)-**1**. Interestingly, the same Cu^{II} product, **8**, is isolated whether Cu(OTf) or Cu(OTf)$_2$ is used in the reaction (Scheme 2). Disproportionation of Cu^I (which is in excess) is implicated in the former case. In these metalation reactions, there has been a redistribution of the mono-Schiff base ligand to a salen ligand and free diamine. Similar monoimine disproportionation has been observed by Holbach et al.,[20] and the initial hydrolysis step can be catalyzed by base or transition-metal ions,[21] both of which are present under our reaction conditions.

Structural Characterization. Table 1 summarizes the crystal data for all of the structures collected.

The hydrogen positions obtained from the refinement of the (*R,R*)-**2** structure (Figure 1) indicate that the molecule has an ammonium group as well as a terminal carboxylate that participates in an intramolecular hydrogen bond with the phenol proton. The ammonium C−N and carboxylate C−O bond lengths are consistent with this assignment (Table 2). The molecules are arranged in pleated hydrogen-bonded sheets with no close contacts between sheets and all intermolecular hydrogen bonds being between carboxylate and ammonium groups. Part b of Figure 1 shows the view down b and reveals that the pleats are created by each molecule having two interactions each with two adjacent molecules. In addition, there are hydrogen bonds between adjacent molecules along the cystallographic *b* axis, as revealed by the view down *a* (part c of Figure 1). Table 3 shows the intramolecular and intermolecular hydrogen bonding distances and angles for (*R,R*)-**2**. The structure of the analogous compound with the carboxylic acid group in the 4 position has been recently reported: the same zwitterionic

Table 4. Selected Bond Distances (Angstroms) and Bond Angles (Degrees) for **4**−**7**

	4 (M = Fe)	**5** (M = Co)	**6** (M = Ni)	**7** (M = Zn)
		Bond Angles (°)		
O(22)−M−O(42)	95.60(3)	92.70(7)	95.30(11)	92.59(6)
O(22)−M−N(11)	82.64(2)	88.29(7)	87.78(11)	85.70(6)
O(42)−M−N(11)	92.11(3)	93.44(7)	93.59(11)	93.34(6)
O(22)−M−N(31)	94.86(2)	88.74(7)	88.25(11)	88.89(6)
O(42)−M−N(31)	85.70(3)	85.44(7)	84.50(11)	82.24(6)
N(11)−M−N(31)	176.51(3)	176.78(8)	175.41(12)	172.86(7)
O(22)−M−N(12)	158.28(3)	169.65(7)	167.42(11)	164.86(6)
O(42)−M−N(12)	95.39(3)	84.86(8)	85.32(13)	84.20(7)
N(11)−M−N(12)	78.28(3)	81.83(8)	79.65(12)	79.74(7)
N(31)−M−N(12)	104.61(3)	101.06(8)	104.30(12)	105.27(7)
O(22)−M−N(32)	84.19(3)	91.49(7)	92.78(12)	94.17(7)
O(42)−M−N(32)	164.47(3)	166.54(7)	161.86(11)	161.00(6)
N(11)−M−N(32)	103.24(3)	99.47(7)	102.95(12)	104.85(7)
N(31)−M−N(32)	78.86(3)	81.87(8)	79.53(12)	80.16(7)
N(12)−M−N(32)	90.12(3)	93.16(8)	90.30(13)	93.55(7)
		Bond Distances (Å)		
M−O(22)	2.1284(6)	2.0474(17)	2.049(3)	2.0874(15)
M−O(42)	2.0385(6)	2.0851(16)	2.077(3)	2.1535(15)
M−N(11)	2.1537(7)	2.0383(19)	2.088(3)	2.1223(17)
M−N(31)	2.1326(7)	2.0437(18)	2.094(3)	2.1244(17)
M−N(12)	2.2100(7)	2.094(2)	2.143(3)	2.1482(19)
M−N(32)	2.1952(7)	2.115(2)	2.153(3)	2.1517(19)

form is seen, but a loosely coordinated 1D hydrogen bonding network is produced.[22]

Selected bond lengths and angles for **4**−**7** are provided in Table 4. It is evident that there is little structural difference between the complexes, suggesting that the steric constraints of the ligand strongly direct the observed structure, regardless of the metal ion present. The crystal structures all indicate the formation of double-stranded mononuclear complexes. This is accomplished by the *meridional* coordination of two singly deprotonated tridentate (*R,R*)-**2** ligands. Figure 2 shows the structure of the zinc(II) complex, **7**.[23] Each ligand is coordinated to the zinc via a neutral amine nitrogen, an imine nitrogen, and a phenoxide. The two ligands have a 65.9° angle between them on the basis of the phenyl planes. This is a significant deviation from the 90° angle expected in the absence of steric interactions or chiral directing groups. The primary factor at play here is the directing nature of the chiral cyclohexyl groups, which push the phenyl groups toward each other and close down the interplanar angle between them. The nonlinear C−O−Zn linkages can readily accommodate this arrangement, and there is not a significant steric penalty due to the planar nature of the phenyl groups. The result is a molecule with *M* helicity and a pitch angle of 65.9°, as described by the phenyl groups. This is

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(22) Jeon, Y.-M.; Heo, J.; Mirkin, C. A. *Tetrahedron Lett.* **2007**, *48*, 2591.
(23) Complexes **4**−**6** are isostructural, and details of their structures are provided in the supplementary material.
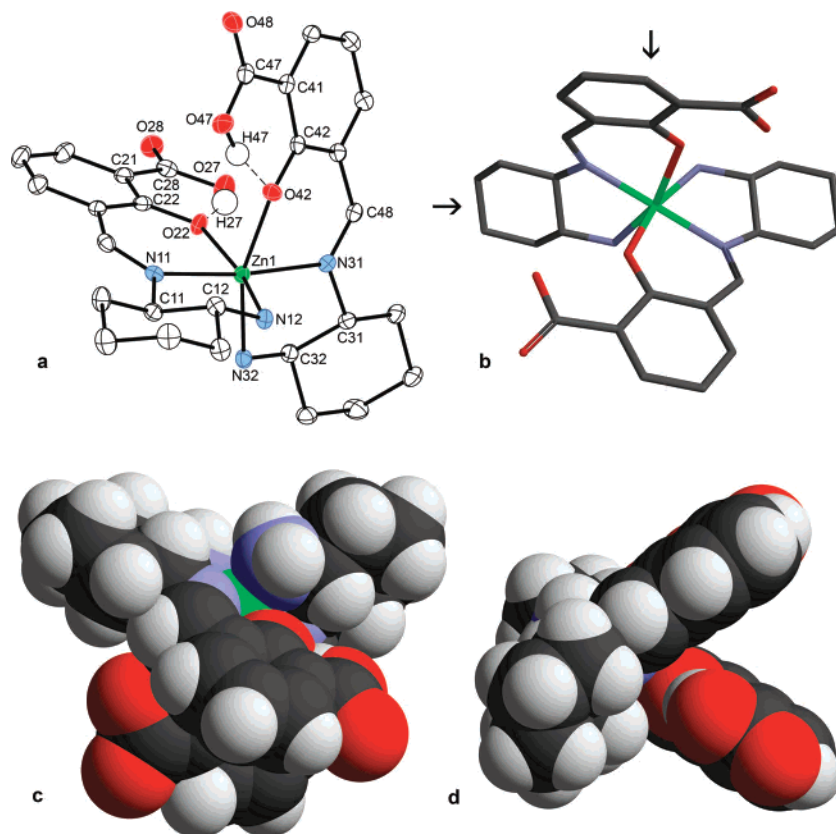
Figure 2. Structure of the zinc(II) complex, **7**: (a) Thermal ellipsoid plot (50%), (b) view down the C_2 axis of the molecule with the approximate directions of view for the space filling plots (c and d) shown.

Table 5. Hydrogen Bonding Distances (Angstroms) and Angles (Degrees) for **4**−**7**

metal	entry	D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	DHA (°)
M = Fe, **4**	1	O(27)−H(27)···O(22)	0.984(15)	1.488(15)	2.4216(8)	156.2(13)
	2	O(47)−H(47)···O(42)	0.842(16)	1.719(16)	2.5046(9)	154.3(18)
	3	N(32)−H(32)···O(48) (B)	0.885(14)	2.197(14)	3.0723(10)	169.9(13)
M = Co, **5**	1	O(27)−H(27)···O(22)	0.91(5)	1.59(5)	2.479(4)	163(5)
	2	O(47)−H(47)···O(42)	0.87(5)	1.56(5)	2.416(4)	168(5)
	3	N(32)−H(32)···O(48) (B)	0.87(5)	2.20(5)	3.072(4)	176(4)
M = Ni, **6**	1	O(27)−H(27)···O(22)	0.88(3)	1.68(3)	2.482(2)	152(3)
	2	O(47)−H(47)···O(42)	0.85(3)	1.60(3)	2.423(2)	165(3)
	3	N(32)−H(32)···O(48) (B)	0.83(3)	2.26(3)	3.092(3)	173(2)
M = Zn, **7**	1	O(27)−H(27)···O(22)	0.78(3)	1.74(3)	2.490(2)	160(3)
	2	O(47)−H(47)···O(42)	0.89(3)	1.55(3)	2.424(2)	165(3)
	3	N(32)−H(32)···O(48) (B)	0.80(3)	2.27(3)	3.059(2)	171(3)

Table 6. Selected Bond Distances (Angstroms) and Bond Angles (Degrees) in **8**

molecule 1	Cu−O(22)	1.909(2)	O(22)−Cu−O(32)	89.30(9)
	Cu−O(32)	1.929(2)	O(22)−Cu−N(12)	176.92(10)
	Cu−N(12)	1.932(3)	O(32)−Cu−N(12)	92.26(10)
	Cu−N(11)	1.943(3)	O(22)−Cu−N(11)	93.58(10)
			O(32)−Cu−N(11)	174.49(10)
			N(12)−Cu−N(11)	85.08(11)
molecule 2	Cu−O(22)	1.908(2)	O(22)−Cu−O(32)	88.80(9)
	Cu−O(32)	1.920(2)	O(22)−Cu−N(12)	174.49(9)
	Cu−N(12)	1.936(3)	O(32)−Cu−N(12)	93.43(9)
	Cu−N(11)	1.938(3)	O(22)−Cu−N(11)	92.38(10)
			O(32)−Cu−N(11)	176.06(9)
			N(12)−Cu−N(11)	85.74(11)

significantly different from the structures of most other *mer*-[M(ABC)$_2$] systems, where there is little deviation from octahedral geometry[5−9] except in the presence of high steric congestion at the metal center.[5,9]

The crystal structures of **4**−**7** reveal that the individual molecules are arranged in *M*-helical strands, formed by N−H···O interactions between molecules (Figure 3). Table 5 (entry 3) lists the intermolecular hydrogen-bonding distances and angles of the complexes. Hydrogen bonding interactions between the amine donors and the carboxylic acid acceptors of adjacent molecules produces one-dimensional *M*-helices of molecules along the crystallographic *b* axis. One of the ligands of a given molecule participates in intermolecular hydrogen bonds, whereas the other does not and forms angled blades in the helix. There is no hydrogen bonding between the helical strands.

The reaction of (*R,R*)-**2** with copper salts resulted in a completely different structure than those seen for the other metals examined. Figure 4 shows the structure of **8**, and Table 6 contains selected bond distances and angles. The
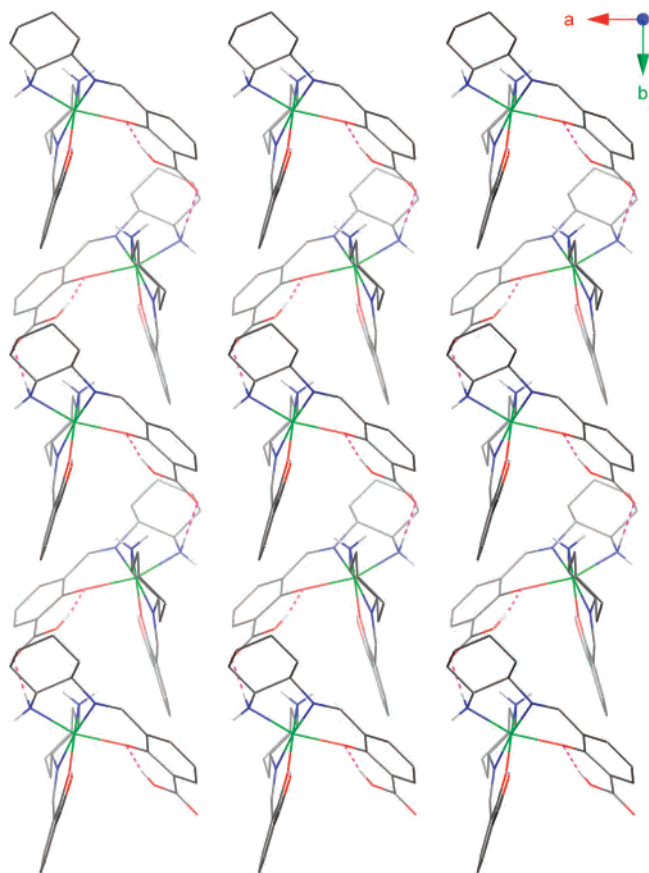
Figure 3. Crystal packing diagram for **4** showing adjacent helical strands of hydrogen-bonded molecules.
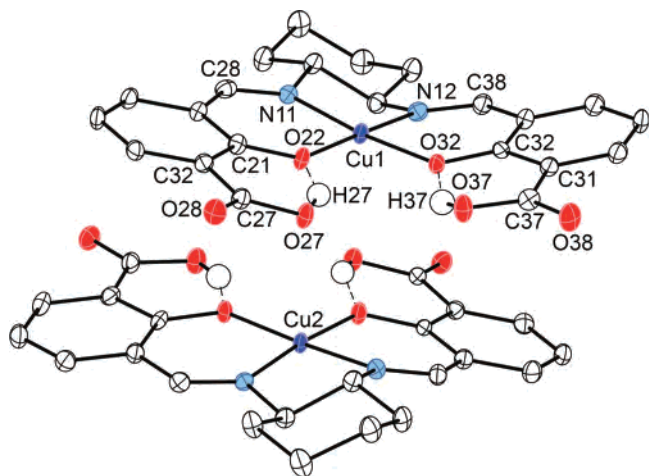

Figure 4. Thermal ellipsoid plot (50%) for **8**.

copper ion is complexed to the dianion of the tetradentate ligand (*R,R*)-**1**, which has reformed from (*R,R*)-**2**. The result is a salen complex with terminal carboxylic acid groups, the protons of which are hydrogen-bonded to the phenoxide donors (Table 7). There is an additional hydrogen bond for each molecule between an acid group and a methanol of

Table 7. Hydrogen Bonding Distances (Angstroms) and Angles (Degrees) for **8**

D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	DHA (°)
complex 1				
O(27)−H(27)···O(22)	0.84	1.73	2.486(4)	149.4
O(37)−H(37)···O(32)	0.84	1.73	2.493(3)	149.6
O(S1)−H(S1)···O(38)	0.84	1.99	2.811(3)	164.9
complex 2				
O′(27)−H′(27)···O′(22)	0.84	1.70	2.476(4)	152.8
O′(37)−H′(37)···O′(32)	0.84	1.72	2.498(3)	152.3
O′(S1)−H′(S1)···O′(38)	0.84	2.01	2.839(3)	166.6

solvation. The coordination at copper is square planar, with only a slight deviation from planarity. There are two very similar molecules in the asymmetric unit that are rotated 180° with respect to one another and stacked parallel. The molecules are cupped away from one another, resulting the breaking of the otherwise C_2 symmetry. Bond lengths and angles are very similar for the two independent molecules.

Conclusions

We have demonstrated the efficient synthesis of a new enantiomerically pure unsymmetrical Schiff-base ligand with a chelating primary amine. This ligand coordinates to a variety of divalent first transition series elements to give *M-meridional* stereoisomers of the type [M(ABC)$_2$]. These are rare examples in which a chiral tridentate ligand forms a single ML$_2$ stereoisomer. These helical molecules are attractive for supramolecular synthesis, owing to the presence of both hydrogen bond donors and acceptors. Indeed, the crystal structures of the complexes all show that extended *M* helices of molecules are assembled by hydrogen bonding interactions between amine and acid groups on adjacent molecules.

Previous studies on unsymmetrical Schiff-base ligands derived from 3-FSA have demonstrated that di- or trinuclear coordination by two ligands are by far the most common modes.[10−16] Whereas complexes of the type [ML$_2$] have been suggested, none have ever been crystallographically characterized until this work. The structures reveal that the carboxylic acid groups do not act as donor groups to the metal ions but are involved in intermolecular hydrogen bonding. Further study of these ligands and complexes, including their solution behavior, is underway.

Supporting Information Available: Full crystallographic details (CIF) as well as thermal ellipsoid plots of **4**−**6** are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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