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Redox-Induced Ligand Reorganization and Helicity Inversion in Copper Complexes of *N,N*-Dialkylmethionine Derivatives

Steffen Zahn, Debasis Das, and James W. Canary*

Department of Chemistry, New York University, New York, New York 10003

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N,N′-Dipicolyl, bis(stilbylvinylpyridylmethyl), and diquinaldyl methionine derivatives form stable Cu^{II} complexes with metal ligation by three nitrogen atoms and the carboxylate. One-electron reduction results in the exchange of carboxylate for sulfide in the complexes. This ligand reorganization is accompanied by inversion of the helical orientation of the two arms containing nitrogen heterocycles, resulting in nearly mirror image circular dichroism spectra. This paper provides details for the synthesis of these complexes and the evidence for the remarkable stereochemical interconversion that accompanies the reduction reaction. Detailed analysis of the electronic spectra of the ligands and metal complexes is provided along with X-ray crystallographic structures of Cu^{II} and Zn^{II} complexes of the *N,N*′-dipicolylmethionine complexes.

Introduction

Chiroptical molecular switches have attracted interest because of a variety of potential applications[1,2] and because of the rich chemistry that such studies have uncovered.[3−6] Our imagination has been captured by redox-triggered molecules, one among many mechanisms in which molecular helicity inversions can be modulated by defined structural processes.[7]

Our approach to this problem grew out of our studies of conformationally biased, labile coordination complexes.[8] Central to these studies was the observation that tripodal ligands with a single chiral center in one of the arms experience a conformational bias affording an additional element of helical chirality. The adopted propellerlike conformation fixes the orientation of appended or inherent chromophores such that the electronic transitions can interact by a coupled oscillator mechanism, resulting in exciton-coupled circular dichroism (ECCD).[9,10]

Additionally, we showed previously that ECCD spectral amplitude could be modulated by one-electron copper redox chemistry, and the spectroscopic change was correlated with conformational dynamics of the ligand in Cu^{I} and Cu^{II} states.[11] Additive effects played a significant role in CD intensity in the system.[12] In essence, we were able to turn the CD signal "on" or "off" by the addition or removal of an electron from a copper ion. It then became of interest to find a way to invert the handedness of the helicity of the complexes by inducing a change in the conformation of the ligand. Such an achievement would result in an electron-triggered "±" ECCD switch, which to our knowledge, is not known outside the present work.[13]

As part of an investigation to develop new methods for the assignment of amino acid absolutes, it was found that amino acids react with bromomethylquinoline to form ligands that complex Cu^{II} and show strong ECCD couplets.[14,15] The CD-active product is illustrated in Figure 1 for the methionine derivative. Tetradentate metallochelates form involving the Cu^{II} ion, the tertiary amine, the two quinolines, and the carboxylate. The stereocenter of the amino acid arm dictates the orientation of the quinoline groups by a "gear" with the

* To whom correspondence should be addressed.

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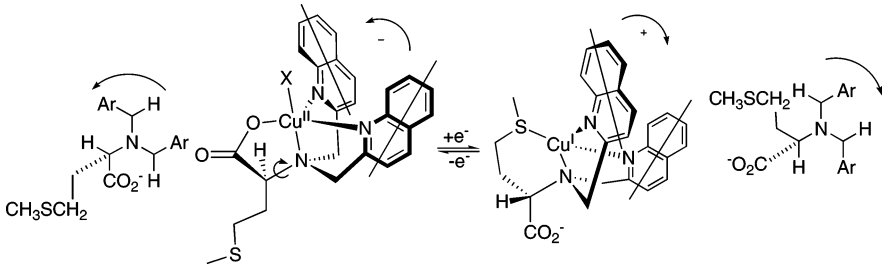

Figure 1. *N,N*-Bis(2-quinolylmethyl)-L-methionine complexes with Cu(II) and Cu(I). The chiral center of the amino acid dictates the orientation of the quinoline chromophores via a gearing mechanism as illustrated. The transition dipoles in the quinolines in the two complexes invert in the sense of absolute orientation and therefore give opposite ECCD spectra.

methylenes of the achiral arms such that a propeller forms from the planar carboxylate and quinoline groups (Figure 1).[16] In consideration of potential alternative ligation modes, the idea surfaced that the Cu^{I} complex might give a propeller complex with the opposite configuration. As shown in Figure 1, for the sulfide to come proximal to the metal center, the amino acid arm must pivot about the C−N bond. This would invert the gearing, and therefore the orientation, of the quinoline moieties, leading to an ECCD couplet with the opposite sign. This approach was successful, and a communication describing our initial work has appeared.[13] Here we discuss our approach in detail, providing synthetic and spectroscopic details plus further structural characterization data that recently became available.

Experimental Section

General Methods.[12] All materials were used as received unless otherwise stated. $[Cu(CH_3CN)_4](PF_6)$ was prepared following the literature method.[17] Cyclic voltammetry experiments were carried out in a standard three-electrode apparatus with a glassy carbon working electrode, a nonaqueous reference electrode (0.1 M $AgNO_3$ in acetonitrile), and a platinum wire auxiliary electrode. Experiments were run in 0.1M *n*-Bu_4NPF_6 as supporting electrolyte in acetonitrile. FT-IR spectra for KBr pellets were recorded on a Nicolet 750 spectrophotometer (Magna-IR 750). Electrical conductivity measurements of the complexes at room temperature in acetonitrile solutions were carried out using a YSI conductivity instrument (model 3200) with a YSI dip cell (Model 3256, cell constant 0.1 cm^{-1}), while room-temperature magnetic susceptibility was measured using an MSB-auto magnetic susceptibility balance (Johnson Matthey), which was calibrated with $Hg[Co(SCN)_4]$. A Kratos MALDI-TOF I mass spectrometer using the matrix α-ACHC and an extraction voltage of 4 kV was used for mass spectrometry. Calculated structures were generated using SPARTAN software,[18] with MMFF94 used to search for conformations and PM3 with geometry optimization to minimize coordination complexes. Unless otherwise stated, UV−vis spectra (5μM) and CD spectra (0.3 mM, 0.1 cm path length) were taken at ambient temperature in methanol. Optical rotations were determined on a Perkin-Elmer model 341 polarimeter at 589 nm.

(*S*)-*N,N*−Bis(2-pyridylmethyl)methionine Methyl Ester ((*S*)-3a). 2-Picolyl chloride hydrochloride (8.21 g, 50.05 mmol) was dissolved in 60 mL of DMF. To this solution, L-methionine methyl ester hydrochloride (5.0 g, 25 mmol) was added followed by $NaHCO_3$ (13 g, 155 mmol). The resulting mixture was heated to 110−112 °C for 24 h. Upon evaporation of solvent, the residual solid was dissolved in water/methylene chloride. The organic layer was collected by extractive isolation, dried over anhydrous K_2CO_3, and subjected to column chromatography (ethyl acetate/methylene chloride = 1:1) to yield 4.25 g (50%) of the title compound as a red oil. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.98 (3H, s, CH_3); 2.01 (2H, m, CH_2); 2.52 (2H, m, CH_2); 3.60 (1H, t, CH, J_{CH-CH2} = 6.84 Hz); 3.74 (3H, s, CH_3); 3.98 (4H, s, CH_2); 7.12 (2H, m, H-3); 7.45 (2H, m, H-5); 7.49 (2H, m, H-4); 8.50 (2H, d, H-6, $J_{5,6}$ = 4.76 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 15.45, 29.46, 31.11, 51.71, 57.55, 61.81, 122.13, 123.01, 136.53, 149.12, 159.61, 173.21. MS (*m*/*e*): 345.8 $(M+H)^+$. $[\alpha]^{21}_D = -50°$ (*c* 0.086, acetonitrile).

(*S*)-*N,N*-Bis(2-pyridylmethyl)methionine ((*S*)-4a). To a solution of *(S)*-**3a** (5.5 g, 16 mmol in 50 mL THF), 0.5 N aqueous LiOH (20 mL) solution was added under stirring at room temperature. The stirring was continued for 4 h. The solvent was removed under reduced pressure. The residue was dissolved in water and extracted with dichloromethane to remove impurities or unreacted ester. The pH of the aqueous portion was adjusted to 7.0−7.5 with dilute HCl and then extracted with ethyl acetate. Traces of water were removed with anhydrous Na_2CO_3. The solvent was removed under reduced pressure, and the residue was subjected to silica gel column chromatography. The desired compound was eluted with methanol/acetone (1:1). The product (1.8 g, 35%) was hygroscopic. mp: 62 ± 1 °C. ^{1}H-NMR (200 MHz, $CDCl_3$, peaks in this spectrum are relatively broad): δ 1.93 (2H, m, CH_2); 2.15 (3H, s, CH_3); 2.45 (2H, m, CH_2); 3.25 (1H, t, J = 7 Hz, CH); 3.88 (4H, s, CH_2); 7.08 (6H, m); 7.55 (2H, m). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 15.97, 26.87, 34.13, 56.14, 64.28, 122.66, 123.10, 137.49, 150.92, 159.04 (H-2). MS (*m*/*e*): 332.1 $(M + H)^+$. Anal. Calcd for $C_{17}H_{21}N_3O_2SNa\cdot 1.5\ H_2O$: C, 53.60; H, 6.04; N, 11.04. Found: C, 53.50; H, 5.98; N, 10.98. FT-IR data (cm^{-1}): ν 1622 (CO); 1597 (C═N); 3392 (OH). $[\alpha]^{21}_D = -51.6°$ (*c* 0.256, acetonitrile).

(*R*)-**3a**, $[\alpha]^{21}_D = +51°$ (*c* 0.068, acetonitrile) and (*R*)-**4a**, mp: 58 ± 1 °C. $[\alpha]^{21}_D = +64°$ (*c* 0.033, acetonitrile). Yields were comparable to those for *(S)*-isomers.

[Zn(4a)]ClO_4. (***Caution!*** *Perchlorate salts of metal complexes with organic ligands are potentially explosive. They should be handled in small quantities and with caution.*)[19] To a methanolic solution of $Zn(ClO_4)_2\cdot 6H_2O$ (56.2 mg, 0.151 mmol in 10 mL methanol) was added a solution of **4a** (49.95 mg, 0.151 mmol in 10 mL methanol) and stirred for 30 min. An off-white precipitate was filtered under suction and dried under vacuum to yield 59.8 mg (80%) of the complex. Crystals suitable for X-ray diffraction studies were obtained from methanol/water by slow evaporation. ^{1}H NMR (CD_3CN, 200 MHz): δ 2.1 (3H, s, CH_3); 2.3 (2H, m, CH_2); 2.52 (2H, m, CH_2); 3.3 (1H, t, CH, J_{CH-CH2} = 6.84 Hz);

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3.75 (1H, d, CH_2, J_{gem} = 16.78 Hz); 3.96 (1H, d, CH_2, J_{gem} = 16.56 Hz); 4.26 (1H, d, CH_2, J_{gem} = 16.20 Hz); 4.34 (1H, d, CH_2, J_{gem} = 16.62 Hz); 7.56 (4H, m, H-4, H-3); 8.10 (2H, m, H-5); 8.60 (2H, m, H-6). Anal. Calcd for $C_{17}H_{20}N_3O_6SZnCl$: C, 41.22; H, 4.04; N, 8.49. Found: C, 41.30; H, 3.97; N, 8.32. FT-IR (cm^{-1}): ν 1611 (CO); 1562 (C═N); 1099 (ClO_4). MS (*m*/*e*): 395.6 $(ZnL)^+$.

[Cu(4a)]ClO_4. This compound was prepared in a manner similar to above except that $Cu(ClO_4)_2 \cdot 6H_2O$ (55.95 mg, 0.151 mmol in methanol) was used in place of $Zn(ClO_4)_2 \cdot 6H_2O$. The complex was green in color. Anal. Calcd for $C_{17}H_{20}N_3O_6SCuCl$: C, 41.38; H, 4.06; N, 8.52. Found: C, 41.19; H, 3.93; N, 8.23. FT-IR (cm^{-1}): ν 1608 (CO); 1575 (C═N); 1098 (ClO_4). MS (*m*/*e*): 393.6 $(CuL)^+$. Crystals suitable for X-ray diffraction studies were obtained from methanol/water by slow evaporation.

(*S*)-*N*,*N*-Bis(2-quinolylmethyl)methionine Methyl Ester ((*S*)-3b. To 60 mL of DMF were added 2-bromomethylquinoline[20] (8.82 g, 39.7 mmol), L-methionine methyl ester (3.96 mg, 19.8 mmol), and sodium bicarbonate (7.5 g, 89.3 mmol). The mixture was stirred at 70−80 °C for 4 h. Upon evaporation of the solvent, a solid remained which was dissolved in a water/methylene chloride mixture. The organic layer was collected, dried over potassium carbonate, and subjected to column chromatography (EtOAc/CH_2Cl_2 1:1) to yield 8.0 g (91%) of the title compound. Anal. Calcd for $C_{26}H_{27}N_3O_2S$: C, 70.08; H, 6.10; N, 9.43. Found: C, 70.03; H, 6.00; N, 9.30; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.99 (3H, s, CH_3); 2.12 (3H, m, CH_2); 2.63 (2H, m, CH_2); 3.74 (1H, t, CH, J_{CH-CH2} = 6.84 Hz); 3.79 (3H,s, CH_3); 4.25 (4H, s, CH_2); 7.49 (2H, m, H-3); 7.6 (2H, d, H-5, $J_{5,6}$ = 8.58 Hz); 7.7 (4H, m, H-6, H-7); 8.07 (4H, d, H-4, H-8, J = 8.44 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 15.80 (CH_3); 29.93 (CH_2); 31.61 (CH_2); 52.11 (OCH_3); 58.8 (CH_2); 62.85 (CH); 121.49; 126.6; 127.74; 127.88; 129.51; 129.79; 136.71; 148.01; 160.51; 173.86 (carbonyl). MS (*m*/*e*): 446.5 (M + H^+).

(*S*)-*N*,*N*-Bis(2-quinolylmethyl)methionine ((*S*)-4b). To 7 g (15.7 mmol) of (*S*)-**3b** dissolved in 45 mL of THF was added 45 mL of a 0.5 N aqueous lithium hydroxide solution. The mixture was stirred at room temperature for 2 h. Upon evaporation of the solvent, the remaining solid was dissolved in water. The pH of the aqueous solution was carefully brought to 6.5−7 with dilute HCl and extracted with several portions of methylene chloride. The combined organic layers were collected, dried over sodium sulfate, and subjected to column chromatography (EtOAc) to yield 5.4 g (80%) of the title compound. Anal. Calcd for $C_{25}H_{25}N_3O_2S$: C, 69.57; H, 5.83; N, 9.73. Found: C, 69.38; H, 5.82; N, 9.48; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 2.1 (3H, s, CH_3); 2.15 (1H, m, CH_2); 2.48 (1H, m, CH_2); 2.78 (2H, m, CH_2); 4.0 (1H, dd, CH, J_{CH-CH2} = 6.22 Hz); 4.4 (4H, s, CH_2); 7.37 (2H, d, H-3, J_{3-4} = 8.4 Hz); 7.53 (2H, m, H-6); 7.73 (4H, m, H-5, H-7); 8.05 (2H, d, H-4, J_{4-3} = 8.4 Hz); 8.15 (2H, d, H-8, $J_{8,7}$ = 9.04 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 15.86 (CH_3); 28.78 (CH_2); 32.11 (CH_2); 57.48 (CH_2); 65.11 (CH); 121.01; 126.94; 127.76; 127.97; 128.59; 130.34; 137.58; 147.24; 160.29; 176.14 (carbonyl). MS (*m*/*e*): 432.54 (M + H^+).

(*S*)-*N*,*N*-Bis-(6-[2-(4-styryl-phenyl)-vinyl]-pyridin-2-ylmethyl)-methionine *tert*-Butyl Ester ((*S*)-3c). To 3.95 g (14.96 mmol) of 2,6-bisbromomethylpyridine dissolved in 70 mL of toluene was added 3.95 g (15.07 mmol) of PPh_3. The mixture was refluxed for 2 h, and a white precipitate formed gradually. The precipitate was collected, washed with toluene, and dried to yield 7.3 g (93%) of the Wittig salt.

Trans-stilbene-4-carboxaldehyde (2.33 g, 11.2 mmol) dissolved in 40 mL of THF and 5.47 g (10.4 mmol) of the phosphonium salt dissolved in 80 mL of MeOH were combined. To this mixture was added 11 mL of a 1.0 M solution of lithium methoxide. The Wittig product precipitated immediately and was collected after 10 h of stirring, washed with THF, and dried under vacuum to yield 3.8 g (90%) of the pure product.^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.59 (2H, s, CH_2Br); 7.14 (2H, s, CH═CH); 7.3 (6H, m, aromatic and CH═CH); 7.6 (8H, m, aromatic); MS (*m*/*e*): 377.2 (M + H^+).

To 20 mL of DMF were added 2-bromomethyl-6-[2-(4-styryl-phenyl)-vinyl]pyridine (1.25 g, 3.3 mmol), L-methionine *tert*-butyl ester hydrochloride (0.4 g, 1.6 mmol), and sodium bicarbonate (1.25 g, 14.9 mmol). The mixture was stirred at 70−80 °C for 4 h. Upon evaporation of the solvent, the remaining solid was dissolved in a water/methylene chloride mixture. The organic layer was collected, dried over potassium carbonate, and subjected to column chromatography (EtOAc/toluene 1:4) to yield 775 mg (61%) of the title compound. Anal. Calcd for $C_{53}H_{53}N_3O_2S$ C, 79.96; H, 6.71; N, 5.27. Found: C, 80.27; H, 6.71; N, 5.04. ^{1}H NMR (CD_2Cl_2, 200 MHz): δ 1.59 (9H, s, t-Bu); 2.04 (3H, s, CH_3); 2.08 (2H, m, CH_2); 2.69 (2H, m, CH_2); 3.54 (1H, t, CH, J_{CH-CH2} = 7.23 Hz); 4.09 (4H, pair of d, CH_2, J = 14.82 Hz); 7.3 (16H, m, aromatic); 7.6 (16H, m, aromatic). ^{13}C NMR (CD_2Cl_2, 50 MHz): δ 15.96 (CH_3); 29.07 (*t*-Bu-CH_3); 30.35 (CH_2); 31.92 (CH_2); 58.61 (CH_2); 63.94 (CH); 81.96 (*t*-Bu-C); 121.10; 122.12; 127.27; 127.58; 128.19; 128.44; 128.83; 128.90; 129.45; 129.55; 132.56; 137.07; 137.38; 138.03; 138.08, 155.44; 160.73; 172.62 (carbonyl). MS (*m*/*e*): 796.28 (M + H^+).

(*S*)-*N*,*N*-Bis-(6-[2-(4-styryl-phenyl)-vinyl]-pyridin-2-ylmethyl)-methionine ((*S*)-4c). To 500 mg (0.63 mmol) of (*S*)-**3c** dissolved in 5 mL of methylene chloride was added 0.05 mL (72 mg, 0.63 mmol) of TFA. The mixture was stirred at room temperature for 1 h. Upon evaporation of the solvent, the remaining solid was dissolved in water/methylene chloride. The pH of the aqueous solution was carefully brought to 7−7.5 with dilute HCl, and the solution was extracted with several portions of methylene chloride. The combined organic layers were collected, dried over sodium sulfate, and subjected to column chromatography (EtOAc/toluene 1:1) to yield 395 mg (84.9%) of the title compound. Anal. Calcd for $C_{49}H_{45}N_3O_2S$ C, 79.53; H, 6.13; N, 5.67. Found: C, 79.47; H, 6.17; N, 5.39. ^{1}H NMR (CD_2Cl_2, 200 MHz): δ 2.15 (3H, s, CH_3); 2.18 (1H, m, CH_2); 2.73 (3H, m, CH_2); 3.89 (1H, t, CH, J_{CH-CH2} = 7.34 Hz); 4.33 (4H, pair of d, CH_2, J = 15.38 Hz); 7.02 (2H, d, CH═CH, J = 12.38 Hz); 7.33 (26H, m, aromatic); 7.76 (2H, d, aromatic, J = 8.44 Hz); 8.04 (2H, t, aromatic, J = 8.44 Hz). ^{13}C NMR (CD_2Cl_2, 50 MHz): δ 15.94 (CH_3); 30.13 (CH_2); 31.90 (CH_2); 58.59 (CH_2); 64.90 (CH); 120.70; 121.71; 126.86; 127.17; 127.79; 128.04; 128.42; 128.48; 129.04; 129.14; 132.15; 136.65; 136.99; 137.62; 137.67; 155.02; 160.32; 177.23 (carbonyl). MS (*m*/*e*): 740.7 (M + H^+).

Cu^{II}((*S*)-4b)(ClO_4). A solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (450 mg, 1.21 mmol) in 2 mL of MeOH was added via pipet to a solution of (*S*)-**4b** (500 mg, 1.16 mmol) in 10 mL of methanol. A blue-green precipitate formed immediately. The product was filtered, washed with diethyl ether, and dried under vacuum to yield 612 mg (89%) of the complex. mp 189 °C (dec); Anal. Calcd for $C_{25}H_{24}N_3O_6SCuCl$: C, 50.58; H, 4.07; N, 7.07. Found: C, 50.44; H, 3.95; N, 6.92. MS (*m*/*e*): 494.2 (CuL^+).

Zn^{II}((*S*)-4b)(ClO_4). A solution of $Zn(ClO_4)_2 \cdot 6H_2O$ (277 mg, 0.75 mmol) in 6 mL of MeOH was added via pipet to a solution of (*S*)-**4b** (220 mg, 0.51 mmol) in 6 mL of methanol. A white precipitate formed immediately. The product was filtered, washed with diethyl ether, and dried under vacuum to yield 200 mg (68%)

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of the complex. mp 201°C (dec); Anal. Calcd for $C_{24}H_{24}N_3O_6SZnCl$: C, 49.41; H, 4.14; N, 7.20. Found: C, 49.29; H, 3.96; N, 6.93. MS (*m*/*e*): 495.8 (CuL^+).

Cu^{II}((L)-3b)$(ClO_4)_2$. A solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (600 mg, 1.62 mmol) in 2 mL of MeOH was added via pipet to a solution of **3b** (700 mg, 1.57 mmol) in 5 mL of methanol. A green-blue precipitate formed immediately. The product was filtered, washed with diethyl ether, and dried under vacuum to yield 700 mg (63%) of the complex. mp 156 °C (dec). Anal. Calcd for $C_{26}H_{27}N_3O_{10}SCuCl_2$: C, 44.11; H, 3.84; N, 5.93. Found: C, 43.92; H, 3.65; N, 6.08. MS (*m*/*e*): 509.3 (CuL^+).

Cu^{I}((*S*)-3b)PF_6. Freshly distilled CH_2Cl_2 (15 mL) was added to **(*S*)**-3b (170 mg, 0.38 mmol) and $[Cu(MeCN)_4]PF_6$ (137 mg, 0.37 mmol) in an inert glovebox. The solids gradually dissolved, and the solution became yellow. The yellow solution was allowed to stir for 15 min. Dry diethyl ether (70 mL) was used to precipitate a yellow solid. After filtration, the solid was washed with dry diethyl ether and dried under vacuum, resulting in 180 mg (72%) of the yellow product. mp 128 °C (dec). Anal. Calcd for $C_{26}H_{27}N_3O_2SCuPF_6$: C, 47.74; H, 4.16; N, 6.42. Found: C, 47.61; H, 4.08; N, 6.17. MS (*m*/*e*): 509.5 (CuL^+). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 2.21 (3H, s, CH_3); 2.36 (2H, m, CH_2); 2.62 (1H, m, CH_2); 3.02 (1H, m, CH_2); 3.7 (1H, m, CH); 3.9 (3H, s, OCH_3); 4.05 (1H, d, CH_2, J = 16.8 Hz); 4.67 (1H, d, CH_2, J = 16.8 Hz); 4.79 (2H, pair of d, CH_2, J = 17.9 Hz); 7.59 (4H, m, aromatic); 7.89 (4H, m, aromatic); 8.33 (3H, m, aromatic); 8.59(1H, d, J = 8.14 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 19.95 (CH_3); 26.01 (CH_2); 36.8 (CH_2); 53.3 (OCH_3); 56.36 (CH_2); 61.8 (CH_2); 68.05 (CH); 121.72; 122.04; 128.11; 128.23; 128.82; 129.00; 129.10; 131.75; 132.12; 139.15; 139.44; 145.77; 146.22; 157.96; 158.46; 171.03 (carbonyl). ^{1}H NMR (CD_2Cl_2, 200 MHz): δ 2.23 (3H, s, CH_3); 2.36 (2H, m, CH_2); 2.70 (1H, m, CH_2); 3.07 (1H, m, CH_2); 3.75 (1H, m, CH); 3.9 (3H, s, OCH_3); 4.09 (1H, d, CH_2, J = 16.84 Hz); 4.62 (1H, d, CH_2, J = 16.84 Hz); 4.8 (2H, pair of d, CH_2, J = 17.92 Hz); 7.45 (1H, d, aromatic, J = 4.4 Hz); 7.65 (3H, m, aromatic); 7.95 (4H, m, aromatic); 8.39 (3H, m, aromatic); 8.64 (1H, d, J = 8.42 Hz).

Cu^{I}((*S*)-4b)PF_6. Freshly distilled CH_2Cl_2 (10 mL) was added to (*S*)-**4b** (100 mg, 0.23 mmol) and $[Cu(MeCN)_4]PF_6$ (85 mg, 0.22 mmol) in a glovebox. The solids gradually dissolved, and the solution became yellow. The yellow solution was allowed to stir for 15 min. Dry diethyl ether (50 mL) was used to precipitate a yellow solid. After filtration, the solid was washed with dry diethyl ether and dried under vacuum, resulting in 122 mg (82%) of the yellow product. mp 162 °C (dec); Anal. Calcd for $C_{25}H_{25}N_3O_2SCuPF_6$: C, 46.91; H, 3.94; N, 6.57. Found: C, 46.95; H, 3.93; N, 6.31. MS (*m*/*e*): 495.0 (CuL^+). ^{1}H NMR (CD_2Cl_2, 200 MHz): δ 2.26 (3H, s, CH_3); 2.45 (2H, m, CH_2); 2.76 (1H, m, CH_2); 3.1 (1H, m, CH_2); 3.87 (1H, m, CH); 4.13 (1H, d, CH_2, J = 15.62 Hz); 4.8−5.0 (3H, m, CH_2); 7.54 (1H, m, aromatic); 7.72 (3H, m, aromatic); 7.95 (4H, m, aromatic); 8.41 (3H, t, aromatic); 8.66 (1H, d, J = 7.7 Hz).

Cu^{II}((*S*)-4c)ClO_4. A solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (300 mg, 0.81 mmol) in 2 mL of MeOH was added via pipet to a solution of (*S*)-**4c** (595 mg, 0.805 mmol) in 10 mL of methylene chloride. A yellow precipitate formed immediately upon addition of diethyl ether (150 mL). The product was filtered, washed with ether, and dried under vacuum to yield 640 mg (87.8%) of the complex. mp 189 °C (dec). Anal. Calcd for $C_{49}H_{44}N_3O_6SCuCl$: C, 65.25; H, 4.91; N, 4.65. Found: C, 65.45; H, 4.91; N, 4.51. MS (*m*/*e*) 802.7 (CuL^+).

Zn^{II}((*S*)-4c)ClO_4. A solution of $Zn(ClO_4)_2 \cdot 6H_2O$ (165 mg, 0.44 mmol) in 2 mL of MeOH was added via pipet to a solution of (*S*)-**4c** (330 mg, 0.44 mmol) in 10 mL of methylene chloride. A yellow precipitate formed immediately upon addition of diethyl ether (150 mL). The product was filtered, washed with diethyl ether, and dried in vacuo to yield 300 mg (74.5%) of the complex. mp 186 °C (dec). Anal. Calcd for $C_{49}H_{44}N_3O_6SZnCl$: C, 65.25; H, 4.91; N, 4.65. Found: C, 65.03; H, 4.80; N, 4.89. MS (*m*/*e*): 804.78 (ZnL^+).

Cu^{I}((*S*)-4c)PF_6. Freshly distilled CH_2Cl_2 (10 mL) was added to (*S*)-**4c** (50 mg, 0.067 mmol) and $[Cu(MeCN)_4]PF_6$ (26 mg, 0.067 mmol) in an inert glovebox. The solids gradually dissolved, and the solution became yellow. The yellow solution was allowed to stir for 15 min. Dry diethyl ether (30 mL) was used to precipitate a yellow solid. After filtration, the solid was washed with dry diethyl ether and dried under vacuum, resulting in 45 mg (71.9%) of the complex. mp 114 °C (dec); Anal. Calcd for $C_{49}H_{45}N_3O_2CuPF_6$: C, 62.05; H, 4.78; N, 4.43. Found: C, 62.13; H, 4.71; N, 4.60. MS (*m*/*e*): 803.8 (CuL^+).

X-ray Crystallographic Analysis. Single-crystal X-ray data of complexes Zn^{II}(**4a**)ClO_4 and Cu^{II}(**4a**)ClO_4 were collected at 173(2) K on a Bruker SMART Platform CCD diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.7107 Å) with a frame time of 25 s and a detector distance of 4.890 (compound Zn^{II}(**4a**)ClO_4) and 4.848 cm (compound Cu^{II}(**4a**)ClO_4). A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrixes determined from 70 and 97 reflections for compound Zn^{II}(**4a**)ClO_4 and Cu^{II}(**4a**)ClO_4, respectively. A randomly oriented region of reciprocal space was surveyed to the extent of 1.5 hemispheres and to a resolution of 0.84 Å. Three major sections of frames were collected with 0.30° steps in ω at three different ϕ settings and a detector position of −28° in 2θ. The intensity data were corrected for absorption and decay (SADABS).[21] Final cell constants were calculated from 2496 (Zn^{II}(**4a**)ClO_4) and 3532 (Cu^{II}(**4a**)ClO_4) strong reflections from the actual data collection after integration.[22]

The structure was solved by using SHELXS-86[23] and refined using SHELXS-97.[23] The space group $P2_1/n$ was determined on the basis of systematic absences and intensity statistics. A direct methods solution was calculated which provides most non-hydrogen atoms from the *E*-map. Full matrix least squares/difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to R1 = 0.0407 and wR2 = 0.1091 (for complex Zn^{II}(**4a**)ClO_4) and R1 = 0.0363 and wR2 = 0.0836 (for complex Cu^{II}(**4a**)ClO_4) (F^2, all data). Crystallographic data and refinements for both complexes are presented in Table 1.

Results and Discussion

Synthesis. Syntheses of the *N*,*N*-bis(arylmethyl) derivatives of L-methionine are shown in Scheme 1. The preparation of the ester derivative **3a**−**c** was carried out in DMF containing $NaHCO_3$ and 2 equiv of **2a**−**c**.[20] Cleavage of the ester moiety of **3a**−**b** was accomplished with aqueous lithium hydroxide. Reaction of the alkylation product of 2,6-dibromopyridine with triphenylphosphine and commercially

(21) Blessing, R. *Acta Crystallogr. A* **1995**, *51*, 33−8.
(22) *SAINT, 6.1*; Bruker Analytical X-ray Systems: Madison, WI.
(23) *SHELXTL-Plus, V5.10*; Bruker Analytical X-ray Systems: Madison, WI.

Scheme 1. Synthesis of the Tripodal Methionine Derivatives and General Structures of Complexes (X = Solvent, Counterion, or Atom from Aggregate in the Solid State)

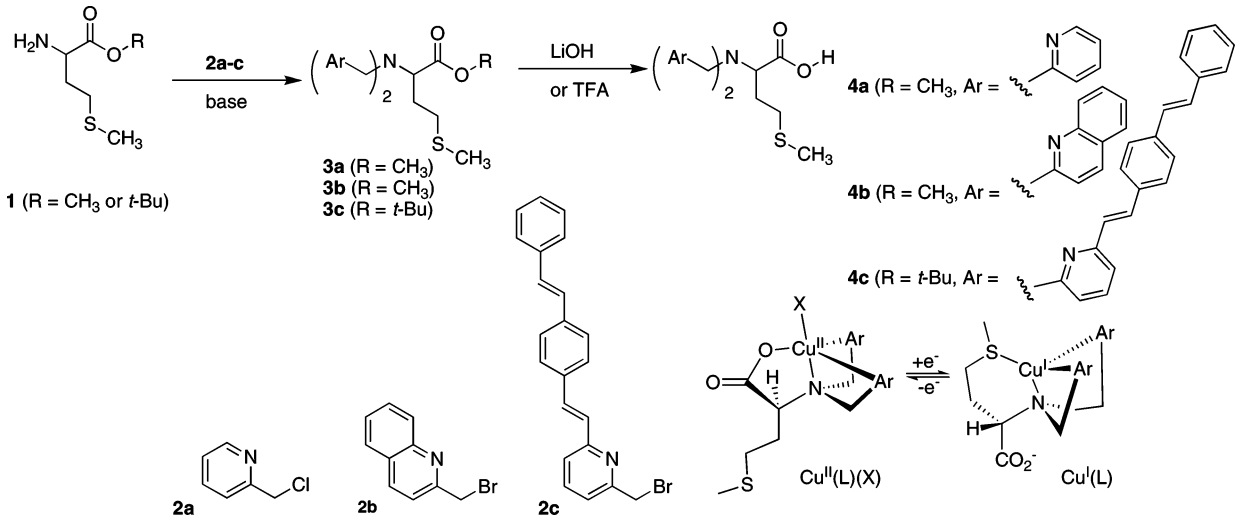

Table 1. Crystal Data and Structure Refinement for Zn^{II}(**4a**)ClO_4 and Cu^{II}(**4a**)ClO_4

	Zn^{II}(**4a**)ClO_4	Cu^{II}(**4a**)ClO_4
empirical formula	$C_{17}H_{20}ClN_3O_6SZn$	$C_{17}H_{20}ClN_3O_6SCu$
fw	495.24	493.41
temp (K)	173	173
cryst color	colorless, block	green, block
cryst dimens	0.22 × 0.12 × 0.10	0.25 × 0.23 × 0.16
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
Z	4	4
a, Å	9.475(2)	9.370(1)
b, Å	9.272(2)	9.308(1)
c, Å	23.973(5)	23.790(3)
α, deg	90.00	90.000
β, deg	100.501(4)	99.374(2)
γ, deg	90.00	90.000
V, Å^3	2070.8(8)	2047.2(4)
ρ (calcd) (g/cm^3)	1.589	1.601
μ (Mo Kα), cm^{-1}	1.455	1.339
F(000)	1016	1012
GOF	1.021	1.005
R1, wR2 $I > 2\sigma(I)$	0.0407, 0.1040	0.0363, 0.0802
all data	0.0537, 0.1091	0.0469, 0.0836

available *trans*-stilbene-4-carboxaldehyde in the presence of $NaHCO_3$ in a 2:1 MeOH/THF mixture provided **3c**. Cleavage of the ester moiety in **3c** was accomplished with TFA. For spectroscopic studies, the coordination complexes were generally prepared by carefully mixing homogeneous solutions of the ligand and the appropriate metal salt.

Structure and Properties of Complexes of 4a. Crystallographic data were obtained that support the Cu(L)(X) structure shown in Scheme 1. Crystals suitable for X-ray diffraction were obtained for the complex Cu^{II}(**4a**)ClO_4 by slow evaporation from methanol/water over several days. An ORTEP[24] view of the complex is shown in Figure 2. In this structure, Cu^{II} possesses a trigonal bipyramidal geometry. The ligand **4a** coordinates to the metal through two pyridine nitrogens, the tertiary amine nitrogen and the deprotonated carboxylate oxygen atoms. Two pyridine nitrogens and one carboxylate oxygen form the trigonal plane with the central copper atom, while a tertiary amino nitrogen and a second carboxylic oxygen from the neighboring molecule occupy the apical positions leading to a one-dimensional helical polymer. The branch containing the sulfur atom is disordered over two positions (85:15), and the perchlorate anion is modeled as disordered over three positions (74:18:8). The intermolecular Cu1−O2 distance (1.927 Å) is smaller than the intramolecular Cu1−O1 distance (2.085 Å), whereas in bis(L-methioninato)copper(II)[25] the opposite trend in respective bond lengths was observed (intramolecular Cu−O1 = 1.944 (8) Å is smaller than intermolecular Cu−O2′ = 2.751 (7) Å bond distance). The structure of the analogous zinc complex was also determined (Supporting Information). The two structures were nearly identical to one another. Although both complexes were obtained in nonracemic form as judged by optical rotation, the crystals that were obtained as suitable for X-ray diffraction were racemic as judged by their centrosymmetric space group (both were $P2_1/n$) and by the lack of optical rotation of dissolved crystals. (Although several methods for quantitation of enantiomeric excess were examined, none proved satisfactory.) The importance of symmetry was described for another interesting tripodal ligand coordination complex.[26]

The room-temperature magnetic moment of the complex Cu(**4a**)ClO_4 is 1.35 μ_B, which is in agreement with the polymeric nature of the complex in the solid state.[27] Measurements of conductances of the acetonitrile solutions of Cu(**4a**)ClO_4 and Zn(**4a**)ClO_4 suggest that they are 1:1 electrolytes, indicating their mononuclear nature in solution, and contrasts the solid-state structures. Unfortunately, satisfactory crystals of Cu^{II} complexes of **4b**−**c** or any Cu^{I} complexes could not be obtained despite several attempts. A crystallographic structure of an alanine analogue of Cu^{II}(**4b**)ClO_4 was published recently, showing a cyclic tetramer that dissociated in acetonitrile solution.[8,28] Thus,

(24) *ORTEP*; Oak Ridge National Laboratory: Oak Ridge, TN.

(25) Ou, C.-C.; Powers, D. A.; Thich, J. A.; Felthouse, T. R.; Hendrickson, D. N.; Potenza, J. A.; Schugar, H. J. *Inorg. Chem.* **1978**, *17*, 34−40.

(26) Xu, X.; Maresca, K. J.; Zahn, S.; Wang, Y.; Das, D.; Zubieta, J.; Canary, J. W. *Chem. Eur. J.* **2002**, *8*, 5679−83.

(27) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; John Wiley and Sons: New York, 1980.

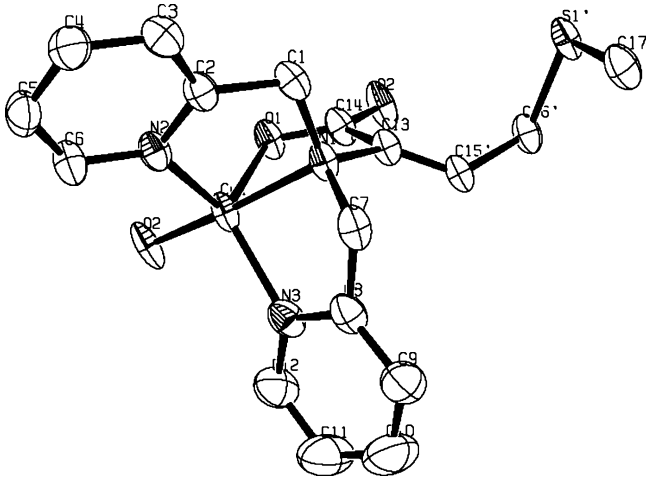

Figure 2. ORTEP view of the cation portion of the complex Cu^{II}(**4a**)ClO_4. Atom O2 from an adjacent complex is included for clarity.

despite the aggregation of the carboxylate complexes in solution, they appear to be dissociated in polar solvents. For data obtained in relatively nonpolar solvents, we do not know if the complexes are aggregated or whether solvent or counterion is coordinated to the metal. No dependence on concentration was observed in CD or ^{1}H NMR spectra. The conformation of the ligand is the same in the aggregated solid-state structures as is proposed for the solution structures.

Absorption and CD Spectra of 4b, 4c, and Complexes. Electronic spectra of **4a** and its metal complexes were recorded in acetonitrile solution at room temperature. The spectra of the ligand shows n$-\pi^*$ (259 nm; $\epsilon = 12\,000$ dm^3 mol^{-1} cm^{-1}) and $\pi-\pi^*$ (203 nm; $\epsilon = 9000$ dm^3 mol^{-1} cm^{-1}) transitions. In the Zn(II) complex, these bands are red-shifted (260 nm; $\epsilon = 7841$ dm^3 mol^{-1} cm^{-1}) and $\pi-\pi^*$ (211 nm; $\epsilon = 7126$ dm^3 mol^{-1} cm^{-1}) due to metalation. In the Cu(II) complex, in addition to the red-shifted transitions (n$-\pi^*$: 261 nm; $\epsilon = 7625$ dm^3 mol^{-1} cm^{-1} and $\pi-\pi^*$: 215 nm; $\epsilon = 11\,389$ dm^3 mol^{-1} cm^{-1}), an additional shoulder at 306 nm ($\epsilon = 1062$ dm^3 mol^{-1} cm^{-1}) may be assigned as a MLCT band. Ligand **4a** and its complexes gave only weak Cotton effects (CEs) with no sign of exciton coupling.

The spectra of the quinoline-containing compounds **4b**, Cu^{II}(**4b**)ClO_4, Cu^{II}(**3b**)$(ClO_4)_2$, Cu^{I}(**3b**)PF_6, and Cu^{I}(**4b**)PF_6 recorded in the ultraviolet region are shown in Figures 3 and 4. Absorption bands can be seen in the regions 320−300, 275, 235, and 205 nm. The maxima have been assigned as ^1L_a (275 nm) (highest occupied to lowest vacant) with degeneracy giving ^1L_b (weak, 315 nm) and ^1B_b (intense, 232 nm). Upon complexation with Cu(II), the ^1B_b bands blue-shift slightly (Cu^{II}, 1 nm; Cu^{I}, 3 nm). Generally, the UV−vis spectra shown here exhibit the same properties as do related compounds, which have been discussed in detail.[12] The free ligand **4b** exhibited almost no CD signal. Introduction of a metal organized the conformationally flexible ligand, affording intense CD signals which display nonconservative, coupled CEs. The sign of the CE depends on both the oxidation state of the copper and the chirality of the ligand. Complexes of ester **3b** give a stronger Cu^{I} CD spectrum (i.e., Cu^{I}(**3b**)PF_6) and very weak Cu^{II} spectrum (i.e., Cu^{II}(**3b**)$(ClO_4)_2$). The presence of the metal effected an expected red-shift in the UV−vis maxima.[9] Complexes Cu^{I}-(**3b**)PF_6 and Cu^{I}(**4b**)PF_6 exhibited CD spectra that fulfill the requirements of ECCD-type spectra, except that the second CE was rather weak. Closer inspection of the UV−vis spectra of these complexes revealed the presence of a transition at 205 nm. Thus, the nonconservative shape of the bisignate CD spectra may be due to overlapping transitions or other nonsymmetric interaction terms.[9,29]

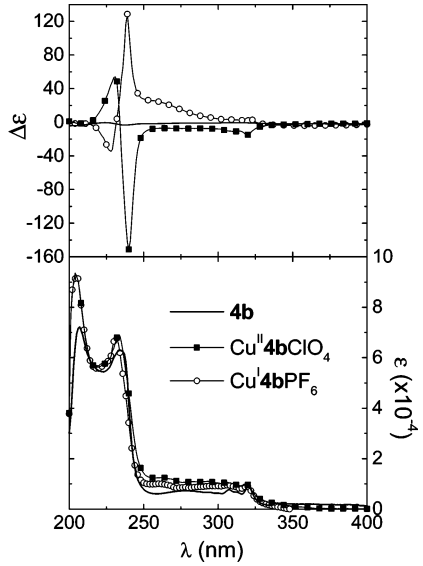

Figure 3. CD (upper) and UV−vis (lower) spectra of ligand **4b** (line), Cu^{I}(**4b**)PF_6 (circles), and Cu^{II}(**4b**)ClO_4 (squares). ϵ and $\Delta\epsilon$ units are L mol^{-1} cm^{-1}.

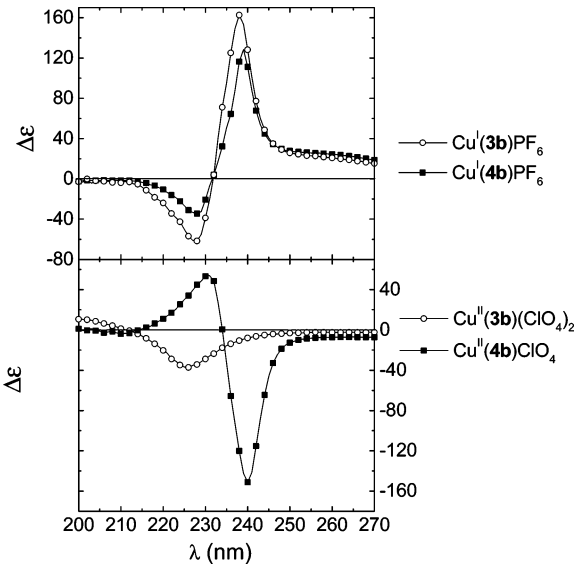

Figure 4. CD spectra of Cu^{I} complexes (upper) and Cu^{II} complexes (lower) of ester **3b** (circles) and acid **4b** (squares). $\Delta\epsilon$ units are L mol^{-1} cm^{-1}.

Calculated structures of Cu^{II}(**4b**)ClO_4 and Cu^{I}(**4b**)PF_6 indicate a counterclockwise disposition (projection angle = −24.5°, distance = 6.4 Å) of the axis of Cu^{II}(**4b**)ClO_4 and

(28) Holmes, A. E., Ph. D., New York University, 2004.

(29) Harada, N.; Nakanishi, K. *Circular Dichroic Spectroscopy: Exciton Coupling in Organic Stereochemistry*; University Science Books: Mill Valley, CA, 1983.

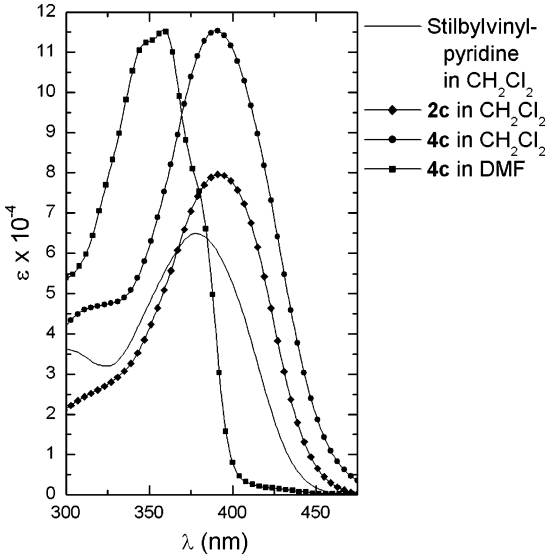

Figure 5. Absorption spectra of stilbylvinylpyridine, bromide **2c**, and ligand **4c**. ϵ units are L mol^{-1} cm^{-1}.

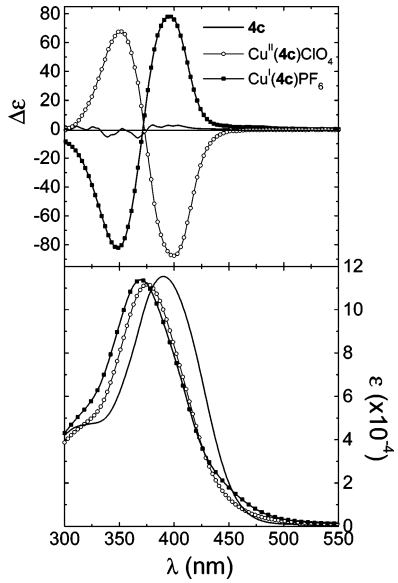

Figure 6. CD (upper) and UV−vis (lower) spectra of ligand **4c** (line), Cu^{I}(**4c**)PF_6 (circles), and Cu^{II}(**4c**)ClO_4 (squares) in methylene chloride. ϵ and $\Delta\epsilon$ units are L mol^{-1} cm^{-1}.

a clockwise disposition (projection angle = +24.5°, distance = 6.4 Å) of the axis of Cu^{I}(**4b**)PF_6. This arrangement should result in a negative exciton coupling for Cu^{II}(**4b**)ClO_4, i.e., the appearance of a negative CE at longer wavelength, followed by a positive CE at shorter wavelength with respect to the corresponding UV−vis transition, and a positive exciton coupling for Cu^{I}(**4b**)PF_6. Indeed, the signs of the CEs were opposite to each other. Furthermore, the observed pairs of CEs with opposite signs for Cu^{II}(**4b**)ClO_4 and Cu^{I}(**4b**)PF_6 are located around their UV−vis peaks, identifying a through-space exciton interaction of strong electric transition moments of the quinolyl chromophores polarized almost parallel to the longitudinal axis.

The splitting occurs for the interaction of the excited states of the adjacent chromophores and is sensitive to the distance between chromophores and the projected dihedral angle.[10] Taking the data obtained from the semiempirical calculation into account, it is therefore rather surprising that the intensities of the spectra of Cu^{II}(**4b**)ClO_4 and Cu^{I}(**4b**)PF_6 differ. This could be due to partial coordination of the carboxylic moiety of the ligand to Cu^{I}. To probe this issue, we prepared the Cu^{I} complex of the ester **3b**. The diminished donor capability of the carboxylate ester in Cu^{I}(**3b**)PF_6 resulted in a stronger CD spectrum. As expected, due to the poor binding properties of the ester moiety of Cu^{II}(**3b**)ClO_4, a weak, distorted CD spectrum was recorded.

To expand the range of wavelengths at which the redox-triggered CD effects could be observed, a chromophore was employed that absorbs visible light. The UV−vis spectrum of stilbylvinylpyridine[30] is plotted in Figure 5. It does not display a fine structure but rather a broad peak that is centered at 378 nm (ϵ = 65 000) in methylene chloride. The brominated derivative **2c** has a similar appearance but is red-shifted to 392 nm (ϵ = 80 000). Ligand **4c** is also featureless in methylene chloride, reaching its absorbance maximum at 390 nm (ϵ = 115 000), whereas in DMF a fine structure emerged. The compound gave rise to a shoulder at 347 nm (ϵ = 112 000), a peak at 359 nm (ϵ = 116 000), and another shoulder around 375 nm (ϵ = 82 000). Upon complexation with copper, substantial shifts toward shorter wavelengths were observed. Complexation with Cu^{I} resulted in a greater shift (20 nm) in the absorbance maximum than with Cu^{II} (15 nm). The CD spectra of **4c**, Cu^{II}(**4c**)ClO_4, and Cu^{I}(**4c**)PF_6 are displayed in Figure 6. Complex Cu^{I}(**4c**)PF_6 exhibits a conservative ECCD curve having the first CE at 398 nm ($\Delta\epsilon$ = +80), followed by a second CE at 348 nm ($\Delta\epsilon$ = −80) of equal intensity and shape. The chiroptical properties of Cu^{II}(**4c**)ClO_4 are nearly mirror-image (first CE = 399 nm, $\Delta\epsilon$ = − 90; second CE = 350 nm, $\Delta\epsilon$ = +70). Thus, the free uncomplexed ligand (**4c**) does not exhibit an ECCD spectrum, whereas the Cu^{II} and Cu^{I} complexes exhibit strong couplets with opposite signs.

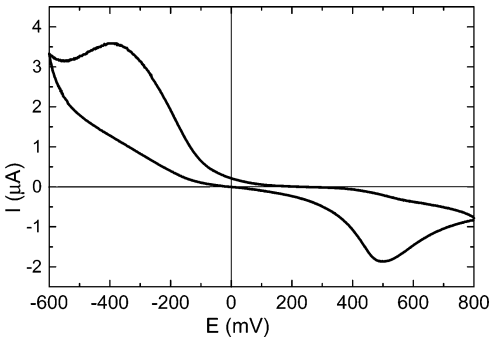

Figure 7. Cyclic voltammogram of Cu^{II}(**4b**)ClO_4.

NMR Studies. ^{1}H NMR spectra were collected in chloroform-*d* and dichloromethane-d_2. Chemical shifts for certain proton resonances of the metal complexes are significantly different compared to the free ligand. The singlet resonance for the methyl (SMe) is shifted in Cu^{I}(**3b**)PF_6 0.22 ppm and in Cu^{I}(**4b**)PF_6 0.16 ppm downfield compared to the free

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ligands **3b** and **4b**. These results are consistent with the structural model involving coordination of the sulfide to the Cu^{I}.

Electrochemistry. A cyclic voltammogram of Cu^{II}(**4b**)-ClO_4 in acetonitrile (MeCN, $E_{pc} = -378$ and $E_{pa} = +492$ mV) is shown in Figure 7. Irreversible behavior was observed, with peak separation of 900 mV (MeCN) at a scan rate of 50 mV s^{-1}. The ferrocene/ferrocenium couple under the same conditions exhibited $\Delta E_p = 100$ mV and $E_{1/2} = 48.3$ mV vs $Ag/AgNO_3$ (MeCN). The complex Cu^{II}(**4a**)ClO_4 behaved similarly (irreversible, glassy carbon, Pt foil, and Ag wire as working, auxiliary, and reference electrodes, respectively, 0.1 M TBAHP, Epc = −219, Epa = +0.51 mV).

The electrochemically irreversible behavior is consistent with significant geometrical changes upon oxidation or reduction. The structural model in Figure 1 shows a mononuclear Cu^{II} complex with a N_3O coordination sphere. In the Cu^{I} complex, the copper ion is ligated by a softer ligand (N_3S). Such large ligand reorganization may certainly lead to irreversible behavior. A more detailed analysis of electrochemical behavior will be presented elsewhere.[31] The electrochemical cycle was repeated more than 20 times without any significant changes in the appearance of the cyclic voltammogram highlighting the reproducibility of the electrochemical cycle.

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Conclusion

We have described the development of a novel system that shows conformational changes resulting in the inversion of chromophoric exciton chirality upon one-electron change. In these propeller-shaped molecules, this spectroscopic phenomenon is best rationalized by the inversion of the axial chiral element defined by the orientation of the two chromophores. In our model, the twist of the propeller is governed by steric factors emerging from the interactions of the amino acid part of the ligand that arise from the different binding preferences for the Cu^{II}/Cu^{I} couple in a well-defined complex. The phenomenon was probed in three different methionine derivatives involving pyridine, substituted pyridine, and quinoline moieties. The stilbene provides a chromophoric system with absorbance at longer wavelength, which provides access to a wide range of experiments and potential applications.

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Supporting Information Available: CIF and ORTEP representation of Zn^{II}(**4a**)ClO_4; CIF for Cu^{II}(**4a**)ClO_4. This material is available free of charge via the Internet at http://pubs.acs.org.

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