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Stereodynamic Coordination Complexes. Dependence of Exciton Coupled Circular Dichroism Spectra on Molecular Conformation and Shape

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Summary. Chiral amino alcohols, amino ethers, and amino thioethers were converted to tetradentate ligands by alkylation with a variety of chromophore-bearing alkyl heterocycles. Copper(II) complexes of the ligands display conformational diastereomerism in solution. The resultant propeller-shaped compounds were characterized by a variety of techniques, including exciton coupled circular dichroism (ECCD). Three X-ray crystal structures of complexes are described that partially support structural assignments, but also suggest that solid state structures are not always indicative of solution species. Thus, ECCD may in some cases provide data that is strongly complimentary to X-ray crystallography. These results are presented in a larger context of coordination complexes that display dynamic behavior that can be studied by chiroptical spectroscopy.

Keywords. Chirality; Circular dichroism; Optical properties; UV-Vis spectroscopy; X-Ray structure determination.

Introduction

In this article, we will briefly summarize features of exciton coupled circular dichroism (ECCD) pertinent to this study; more thorough treatments of the spectroscopy can be found elsewhere [1–3]. We will then provide a brief review of the role that ECCD has played in our laboratory's studies of stereodynamic coordination complexes. Finally, we will present recent results that extend the scope of our methods and provide structural insight regarding the systems studied.

Two chromophores present in a molecule in close proximity to one another may experience interaction of the electronic transitions, resulting in differentiation of the energies of the transitions (Fig. 1). In such a case, two distinct UV-Vis bands may, in principle, be observed, with the difference in energy corresponding to the difference

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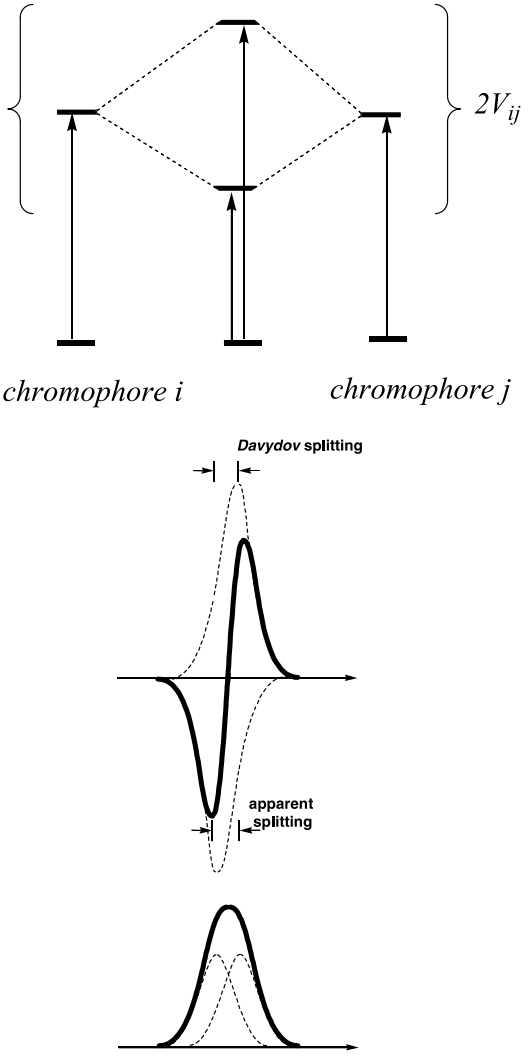


Fig. 1. Exciton interactions give rise to split CD spectra

between the two absorption maxima (λ_{max}). In practice, UV-Vis spectra are broad and two distinct bands are seldom observed. However, in CD spectra, the two coupled absorbances display *Cotton* effects with opposite signs, resulting in sigmoidal shaped curves. Such exciton coupled CD spectra are characterized by the shape of the curve, the large amplitude of the spectrum, and the correspondence of the null in the CD spectrum with the λ_{max} from the UV-Vis spectrum [1, 3, 4]. Few other spectroscopic signals report structural aspects of molecular conformation so dramatically as ECCD. By this feature, ECCD can be used to assign absolute configurations of a variety of organic molecules, since in many cases the conformation of the molecule is known and related to the absolute sense of chirality of the molecule.

Our interest has been drawn to the opportunity to modulate the intensity or sign of the ECCD couplet by coordination chemistry, molecular recognition, or design of compounds with triggered conformations [5]. The amplitude of the ECCD spectrum depends on several factors among which include the strength of the

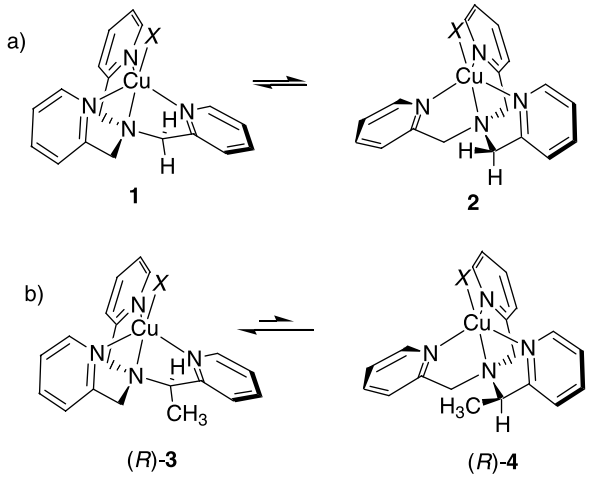


Fig. 2. a) Conformational enantiomerism in tripodal ligand complexes of Cu(II), $X =$ solvent or counter ion; b) incorporation of a single chiral carbon center results in conformational diastereomers

electronic transition, the distance between the chromophores, and the angle between the vectors representing the coupled electronic transition dipoles [1, 3, 4]. Each of these factors is amenable to modulation. In particular, the distance and angle between the chromophores are dependent upon molecular conformation.

Metal complexes of tris(pyridylmethyl)amine (*TPA*) have been studied extensively [6]. This tripodal ligand, which adopts two rapidly interconverting, enantiomeric conformations (Fig. 2, structures **1** and **2**) when bound to Cu(II) or Zn(II), has provided the scaffold upon which a variety of stereodynamic metal complexes has been developed [7]. Incorporation of a single chiral center on one of the arms of *TPA* creates an analogous pair of conformational diastereomers, as in structures **3** and **4** of Fig. 2. The pyridines adopt a propeller-like orientation, the direction of which is dictated by the methyl substituent, with the metal and the tertiary nitrogen forming the axis. In this case, the equilibrium is shifted toward the left-handed propeller because the methyl substituent points away from the pyridyl group [8].

When pyridines are replaced by quinolines, these complexes give strong ECCD spectra [7, 9]. Figure 3 illustrates compound **5**, which as a free ligand exists in many conformations and therefore gives a weak CD spectrum. Upon complexation with Zn(II), the ligand wraps around the metal ion, and the quinoline chromophores are fixed in an orientation that gives rise to a strong ECCD couplet. The sign of the ECCD couplet reveals the absolute sense of orientation of the quinoline moieties, and therefore the handedness of the propeller. Since the propeller configuration depends on the absolute configuration of the chiral carbon center, the latter can be assigned from the sign of the ECCD couplet. An X-ray crystallographic structure of **6** (Fig. 3) corroborated the solution CD spectrum. Since then, many other crystallographic structures of similar complexes coupled with solution CD studies have set our understanding of conformations in pyridine and quinoline tripodal ligand complexes on firm ground [10]. Zn(II) and Cu(II) complexes give similar CD spectra because they typically form 5-coordinate, trigonal bipyramidal structures with these tripodal ligands. Octahedral metals, such as Cd(II) and Fe(II),

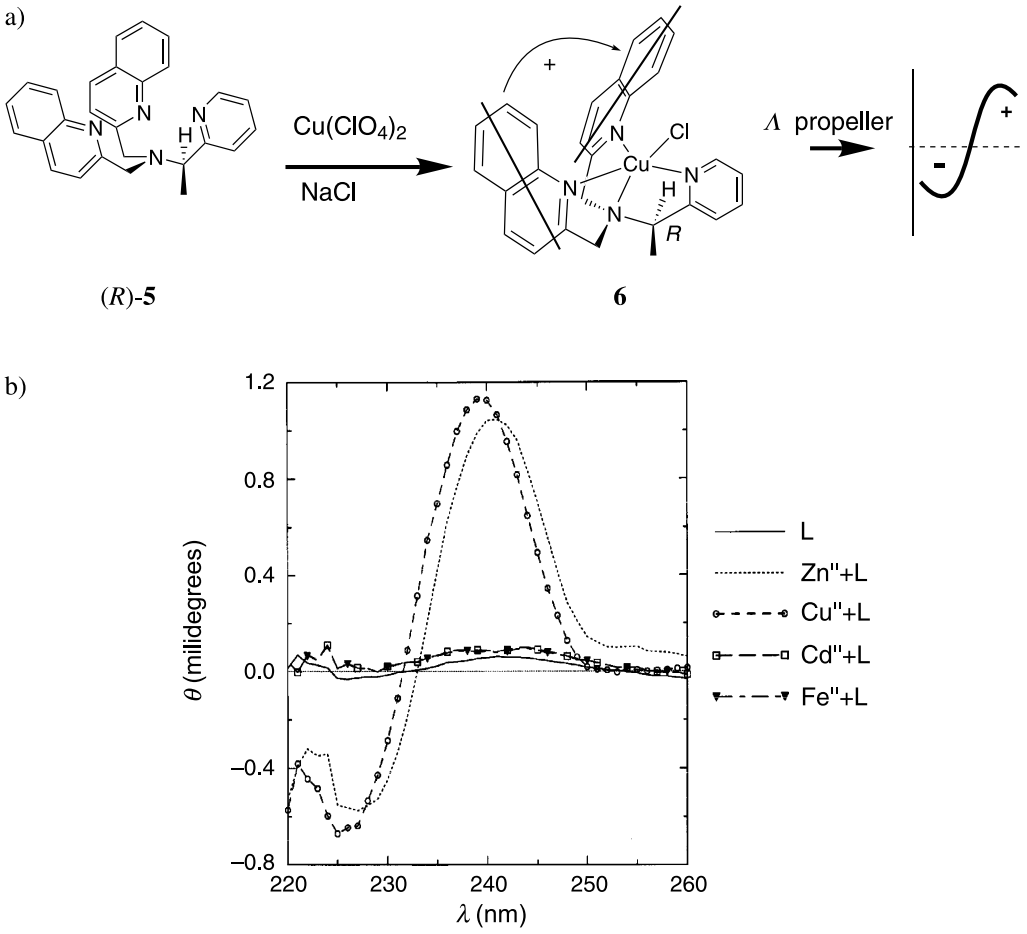


Fig. 3. a) Free ligand **5** may obtain many conformations; complexation to Cu(II) causes the ligand to wrap around the metal ion, adopting a propeller shape, and orienting the quinoline chromophores for ECCD; b) CD spectra of **5** and Cu(II), Zn(II), Cd(II), and Fe(II) complexes of ligand **5**, mM solutions in water; only Cu(II) and Zn(II) complexes give ECCD spectra

may not give the proper orientation for ECCD and therefore may not show strong CD spectra as shown in Fig. 3 [11].

We have reported conformational analysis of additional tripodal metal ion complexes **7**–**10** (Fig. 4) using solution, solid state, and computational methods. Various primary amines were alkylated with two chromophores, and complexation to Cu(II) created a conformationally defined, asymmetric species featuring a helical configuration dictated by the absolute configuration of the chiral center. Chiral ligands displayed an *M* (Λ) propeller-like twist when the carbon center was of (*R*) configuration and a *P* (Δ) twist for the (*S*) carbon center. Complex **8** and related compounds were also examined for β, the ability to induce helicity in liquid crystal nematic phase. An intense difference of β between the free ligands and the copper complexes and copper complexed in different oxidation states and with different center ions suggests possible use as liquid crystal display devices [12]. Molecular recognition of various anions was observable in both CD spectra and β determinations.

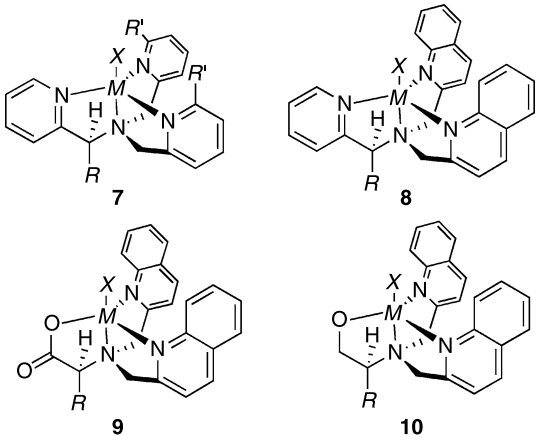
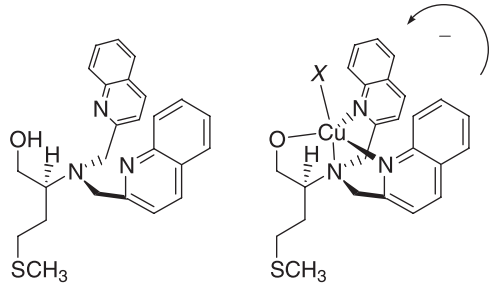


Fig. 4. Tripodal ligands with various alkyl groups and chromophores

One possible application of this research is in the assignment of absolute configurations of chiral primary amines by analysis of ECCD spectra of the derivatives. Derivatization methods with quinoline have shown to work very well with amino acids and alcohols, as in **9** and **10** [11, 13, 14]. A great advantage of the



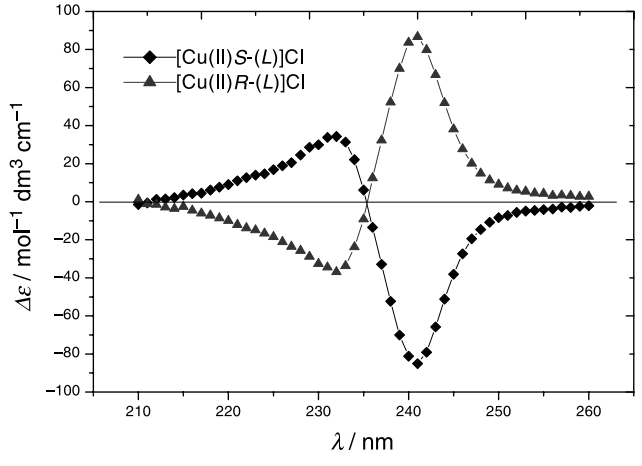
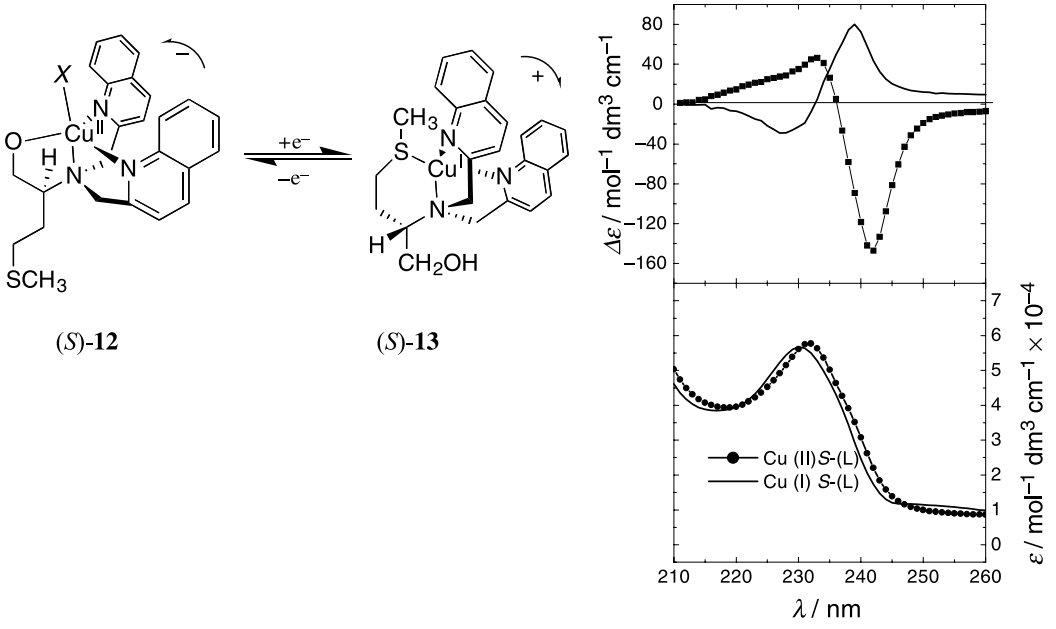


Fig. 5. ECCD spectra of *S*- and *R*-isomers of Cu(II)*L*Cl

derivatization method is the concurrent assessment of enantiopurity because there is a linear agreement between $\Delta\varepsilon$ and *ee*. Figure 5 shows a typical ECCD spectrum for a quinoline derivatized amino alcohol, (*S*)-methioninol, which demonstrates that the negative couplet corresponds to the (*S*)-isomer and the positive couplet to the (*R*)-isomer [15]. Other, complimentary methods have also been reported for assignment of amine absolute configuration by ECCD [16, 17].

Another area that we have examined is the modulation of ECCD amplitude and sign triggered by redox chemistry [18, 19]. Molecular switching devices can be applied in information technology, where chemical devices rely on assuming ''on/off'' states. Helical supramolecular structures, macromolecules, and nanostructures derived from natural or synthetic building blocks that are capable of inverting their handedness upon physical stimulation offer insights into molecular structure and interactions as well as opportunities for device development. The ability to control helicity of supramolecular structures could lead to practical applications in the polymer, electronics, and pharmaceutical industries [20].

Figure 6 depicts the exciton coupled circular dichroism and UV spectra of the Cu(II) and Cu(I) complexes of (*S*)-methioninol derivative Cu(*L*)ClO_4 in methanol [15]. In this figure, the complexes give ECCD spectra that are nearly mirror images of each other. The Cu(II) complex involves coordination by the ligand *via* three nitrogen atoms and an oxygen atom. For the (*S*)-enantiomer, this results in a negative chiral orientation of the chromophores, and gives rise to a (−)-couplet in the ECCD spectrum. The Cu(I) complex displays coordination to the alkyl sulfide arm instead of the alkoxyl group, resulting in the inversion of the twist of the molecule, and yielding a (+)-couplet in the ECCD spectrum. The mirror



(*S*)-**12** (*S*)-**13**

Fig. 6. Redox driven helix inversion; a) ligand reorganization that occurs upon redox reaction (X = solvent or counter ion); b) CD and UV spectra of Cu(I) and Cu(II) complexes

image CD spectrum for the redox isomer arises from inversion of the configuration of the two chromophores, which invert as a result of the pivot of the chiral arm of the tripodal complex. Similar electron-driven chiral inversion was also observed with (*S*)-methyl cysteine and methionine derivatives [21, 22]. The rate of switching was examined recently by scanning electrochemical microscopy and stopped flow circular dichroism [23].

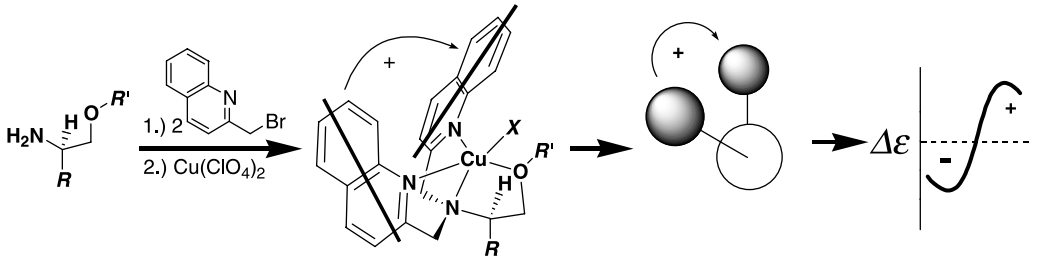
Results and Discussion

In this paper, we report an examination of several β-hydroxy and β-alkoxy amines. Some preliminary data on such compounds were reported in earlier communications [15, 24], but here we describe preparative synthesis and isolation of derivatives and complexes. Amines were reacted with two equivalents of 2-bromomethylquinoline and the product ligand was isolated and purified. Copper complexes were formed by precipitation. Six different, commercially available amines were analyzed, compounds **14a**–**17a**. In each case, split CD spectra were obtained that showed characteristics of ECCD (Table 1). In the UV-Vis spectra, λ_{max} was generally observed near 231 nm with a shoulder near 240 nm. These peaks corresponded closely to the peak and trough in the CD spectra. Similar UV-Vis and CD spectral characteristics were observed in closely related complexes and were assigned to a π–π^* transition with a dipole that corresponds to the longitudinal direction of the quinoline heterocycle [10]. The signs of the ECCD couplets were consistent with the model depicted in Fig. 7. The metal is ligated by the three amine atoms as well as the alcohol or ether side chain moiety, fixing the geometry and giving rise to the ECCD spectrum. In the case of **17**, the oxygen atom of the alcohol moiety out-competes the sulfur atom; if the sulfur atom was coordinated, the opposite ECCD couplet would be observed. The model in Fig. 7 is similar to that proposed for amino acid derivatives [14], but opposite to that reported for primary amine derivatives that lack a coordinating atom in the side chain [25].

The amplitudes of the complexes were reasonably strong, ranging from $A = 90$–180. A smaller amplitude was observed for **14a**, which contains a sterically bulky phenyl substituent that may distort the overall propeller twist, similar to behavior observed previously in a related complex [26]. In order to assess the basis

Table 1. ECCD and UV data for $Cu(L)(ClO_4)_2$ complexes

L	1st *Cotton* Effect $\Delta\varepsilon^{240}$/ $mol^{-1}\,dm^3\,cm^{-1}$	Inflection Point λ/nm	2nd *Cotton* Effect $\Delta\varepsilon^{231}$/ $mol^{-1}\,dm^3\,cm^{-1}$	UV λ_{max}/nm
(*R*)-**14**	13	234	−5	231
(*S*)-**14**	−13	234	5	231
(*R*)-**15**	116	234	−10	231
(*S*)-**15**	−83	234	7	231
(*S*)-**16**	−131	235	50	231
(*R*)-**17**	−41	236	16	228



a **b**

(*R*)-**14** $R = Ph$, $R' = H$ (*R*)-**16** $R = CH_3$, $R' = CH_3$

(*R*)-**15** $R = CH_3$, $R' = H$ (*S*)-**17** $R = PhCH_2SCH_2$, $R' = H$

Fig. 7. Derivatization protocol used in this study; primary amines containing alcohol, ether, or thioether groups were derivatized; a Cu(II) salt was added; the resulting complex gave ECCD spectra that could be used to assign the absolute configuration of the original amine

of the relatively weak CD spectrum of the Cu(**14**) complex, X-ray structures were obtained for the complexes Cu(**14**)$(CH_3CN)(ClO_4)_2$ and $(Cu(\mathbf{14}))_2(BF_4)_2$. The structures are shown in Fig. 8. These complexes both were prepared simply by mixing the requisite copper salts with ligand **14** followed by isolation of the precipitate. However, the two structures are quite different from each other. The perchlorate structure presents the ligand in neutral form. The Cu(II) ion is coordinated by the three nitrogen atoms of **14**, the nitrogen atom of an acetonitrile solvate, and weakly coordinated by an oxygen atom on one perchlorate ($Cu1\cdots O6 = 3.012(4)$ Å). This perchlorate is disordered over two positions in a 30:70 ratio, and 92 restraints were used to force both fragments to have similar

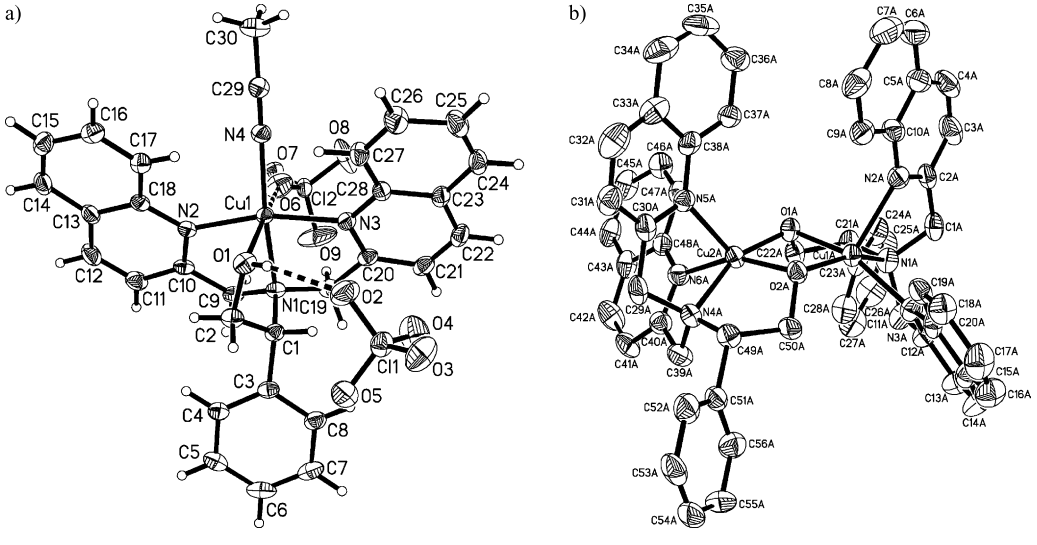


Fig. 8. ORTEP views of X-ray crystallographic structures of Cu(II) complexes of **14**; a) [(*R*)-Cu(**14**)$(CH_3CN)(ClO_4)_2$]; b) [(*S*)-$(Cu(\mathbf{15}))_2$]

bond lengths and bond angles. The hydroxyl is hydrogen bonded to a perchlorate. The two quinoline groups are nearly coplanar in this structure, an orientation that would not be expected to give rise to a strong ECCD couplet. In solution, the structure of the complex would likely differ in that the perchlorate counter ions would be better solvated and would likely be dissociated from the cationic part of the compound in a polar solvent. However, the observed, weak CD spectrum is consistent with a strong proportion of the compound existing in this conformation or a similar one with a non-ideal dihedral angle (for ECCD) between the chromophores.

The BF_4 complex gave a different structure. In this complex, the ligand **14e** crystallized in anionic form, and a dimeric complex resulted with the oxygen atom of the ligand bridging between two copper ions. The conformation of the ligand is similar to that in the model shown in Fig. 7. This structure might therefore be expected to give a stronger ECCD spectrum in solution, but in fact, solutions of this complex gave spectra nearly identical to those prepared from the perchlorate complex. Thus, the solid state structure is probably not representative of the solution structure in this instance.

Another crystallographic structure is shown in Fig. 9 that supports the theme that solid state structures do not always correspond to solution ones. The crystal structure of racemic [Cu(2-(bis(quinolin-2-ylmethyl)amino)propanoate)]ClO_4 (**15a**) is the first X-ray structure of an *N*,*N*-bis(quinolinylmethyl)amino acid derivative (in this case, alanine) that we have been able to obtain, despite many prior attempts [14, 24]. The racemic crystal was prepared by slow diffusion with acetonitrile and methylene chloride. It was necessary to mix equal amounts of the (*R*) and (*S*) isomers to form racemates after many attempts with enantiopure crystals failed to diffract adequately. The tetranuclear cluster contains four copper centers and four ligands that alternate in (*R*) and (*S*) configuration in a cyclic arrangement. The metals are bridged via the carboxylate moieties. The crystal has four-fold symmetry, a coordination number of 5, and a distorted trigonal bipyramidal geometry at the copper center. The atoms O1, N2, and N3 make a rough trigonal plane, while O2 and N1 are the axial ligands. Although there is precedence in the

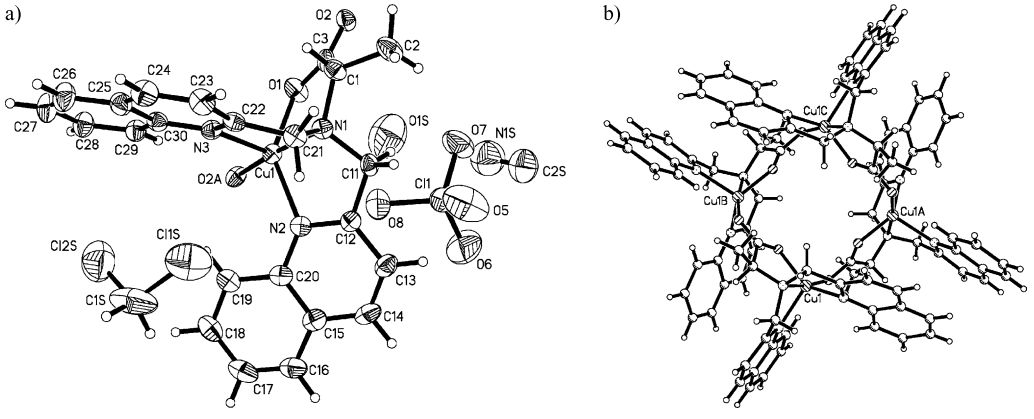


Fig. 9. a) ORTEP view of racemic crystal structure of [Cu(II)-(**9**, R=CH_3)]ClO_4 with distorted trigonal bipyramidal geometry around the copper center; b) tetranuclear cyclic structure adopted in solid state

literature for tetranuclear copper complexes, they are mostly hydroxy-bridged macrocycles and copper bridged pyridines [27, 28]. The observed molecular structure shows the expected ligand conformation in agreement with the model. The carboxylate and three nitrogen atoms coordinate with the metal ion. The propeller twist and orientation of the quinolines relative to the asymmetric carbon center agree with the CD data. Conductivity measurements indicate the aggregate disassociates in acetonitrile solution as demonstrated by a linear relationship between conductivity and molar concentration at 25°C ($R^2 = 0.99$). Whether the aggregate was to persist in solution is not of major concern for the use of these compounds for configurational assignment or chiroptical molecular switches, but it is of interest to note that the solid state structure does not appear to correspond to that found in solution.

Conclusion

ECCD is a unique and powerful spectroscopic tool that can report conformations and stereodynamics in solution. Our work has shown that conformational changes that occur upon metal ion complexation, molecular recognition, and redox cycling can be readily observed by this method. Chiral materials with triggered helical conformations in response to external stimuli, such as electrons as described here, have potential applications in the semiconductor or molecular electronic industry because of their ''on'' and ''off'' states.

The new data reported here serve to extend the repertoire of tripodal, chelating ligands whose Cu(II) complexes give rise to ECCD spectra. The solid state data place the solution structural assignments on firm ground, and point to differences between solid state and solution complexes. The combination of ECCD and X-ray crystallographic characterization can be very fruitful in studies of conformationally mobile systems.

Experimental

The uncorrected melting points were determined on a Mel-Temp II device. Elemental analyses were obtained by Complete Analysis Laboratories Inc, Parsippany, NJ. The 200 MHz ^{1}H and 50 MHz ^{13}C NMR spectra were observed on a Varian Gemini instrument with $CDCl_3$ as solvent. The Maldi-TOF mass spectra were recorded on a Bruker Daltonics Omniflex machine and electron spray ionization spectra on an Agilent Technologies 1100 series machine. Circular dichroism spectra were obtained on an AVIV Stopped Flow Model 202 SF machine.

General Procedures for Synthesis of Free Ligands and Metal Complexes

Procedure A. To 3.24 g of 2-bromomethylquinoline (14.6 mmol) dissolved in 13 cm^3 *DMF* with 2 molar equivalents $NaHCO_3$, the primary amine (7.3 mmol) dissolved in 25 cm^3 *DMF* was added with stirring. The mixture was heated for 4 h to 60–70°C. The *DMF* was evaporated. CH_2Cl_2 (20 cm^3) was added to extract the organic compounds and the organic layer was dried ($MgSO_4$). After the solvent was removed, ethyl acetate was used as the eluent for silica gel column chromatography. The yields varied from 10–49%.

Procedure B. To the primary amine (1 mmol) dissolved in 7 cm^3 of 0.5 *N* NaOH, 0.44 g of 2-bromomethylquinoline (2 mmol) dissolved in ethanol:water (1:1) were added with heating and stirring

forming a white and yellow suspension. After this, 8 cm^3 of 0.5 *N* NaOH were added. The mixture was stirred at 65°C for 1.5 h, and the suspended yellow oil droplets eventually turned red. The reaction mixture was cooled and 15 cm^3 of acetonitrile were added to dissolve the red oil. The reaction mixture was then concentrated by evaporating the solvents. The organic products were dissolved in 25 cm^3 CH_2Cl_2. The solution was washed with 25 cm^3 H_2O and the organic layer was dried ($MgSO_4$). After the solvent was removed, ethyl acetate was used for silica gel chromatography to elute unreacted 2-bromomethylquinoline and then ethyl acetate:acetone (1:1) was used to elute the product.

Procedure for Complex Formation

The free ligand (0.24 mmol) was dissolved in 10 cm^3 of methanol and mixed with 2 cm^3 of an equivalent amount of $Cu(ClO_4)_2$ or Cu(II) tetrafluoroborate. A volume of ether three times the volume of methanol was added and the resulting solution was placed in the refrigerator overnight. The resulting crystals were isolated and dried. The yields for metal complexes varied from 35–68%, depending on the solubility of the complex.

(S)-2-(Bis(quinolin-2-ylmethyl)amino)-2-phenylethanol ((***S***)-**14a**, $C_{28}H_{25}N_3O$)

Procedure A, yield 25%, mp 75–78°C; ^{1}H NMR ($CDCl_3$, CD_3OD, D-*TFA*, 200 MHz): $\delta = 3.8$ (dd, $J_1 = J_2 = 4$ Hz, CH), 4.07 (A of AB, $J = 16$ Hz, CH_2O), 4.0 (s, CH_2O), 4.3 (dd, $J_1 = J_2 = 4$ Hz, CH_2), 4.4 (B of AB, $J = 16$ Hz), 7.32 (m, 2 phenyl-H), 7.36 (m, 3 phenyl-H), 7.45 (t, 4 quinoline-H), 7.65 (m, 4 quinoline-H), 7.8 (d, 2 quinoline-H), 8.1 (d, 2 quinoline-H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 58$, 63, 68, 122, 126, 127, 128, 130, 137, 138, 148, 161 ppm; ESI-MS: $m/z =$ calcd 419.40 ($M + H^+$), found 420.

(R)-2-(Bis(quinolin-2-ylmethyl)amino)-2-phenylethanol ((***R***)-**14a**, $C_{28}H_{25}N_3O$)

Procedure A, yield 49%, mp 75–78°C; ESI-MS: $m/z = 419$ calcd 419.40 ($M + H^+$), found 419.

(S)-2-(Bis(quinolin-2-ylmethyl)amino)-1-propanol ((***S***)-**15a**, $C_{23}H_{23}N_3O$)

Procedure A, yield 10%, CH_2Cl_2:ethyl acetate (1:1) on a silica gel column; ^{1}H NMR ($CDCl_3$, CD_3OD, D-*TFA*, 200 MHz): $\delta = 1.3$ (d, $J = 4$ Hz, CH_3), 3.5 (m, CH), 3.8 (m, CH_2), 3.9 (m, CH_2), 4.3 (A of AB, $J = 12$ Hz, CH_2), 4.5 (B of AB, $J = 12$ Hz, CH_2), 7.7 (t, $J = 8$ Hz, quinoline-H), 8.0 (m, 6 quinoline-H), 8.3 (d, 2 quinoline-H), 8.6 (d, 2 quinoline-H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 10.8$, 56.7, 59.0, 64.6, 121.5, 126.6, 127.7, 127.9, 129.1, 130.0, 136.8, 147.8, 161.1 ppm; ESI-MS: $m/z =$ calcd 358.46 ($M + H^+$), found 358.

(R)-2-(Bis(quinolin-2-ylmethyl)amino)-1-propanol ((***R***)-**15a**, $C_{23}H_{23}N_3O$)

Procedure A, yield 38%, CH_2Cl_2:ethyl acetate (1:1) on a silica gel column.

(S)-1-Methoxy-N,N-bis(quinolin-2-ylmethyl)propan-2-amine ((***S***)-**16a**, $C_{24}H_{25}N_3O$)

Procedure A, yield 43%, CH_2Cl_2:ethyl acetate (1:1) then ethyl acetate:methanol (2:1) on a silica gel column; ^{1}H NMR ($CDCl_3$, CD_3OD, D-*TFA*, 200 MHz): $\delta = 1.2$ (d, $J = 6$ Hz, CH_3), 3.2 (m, CH), 3.3 (s, CH_3O), 3.4 (m, CH_2O), 3.5 (dd, $J = 6$ Hz, NCH_2), 4.4 (dd, $J_1 = 3$ Hz, $J_2 = 6$ Hz, NCH_2), 7.5 (t, 2 quinoline-H), 7.7 (t, 2 quinoline-H), 7.8 (t, 4 quinoline-H), 8.0 (d, 2 quinoline-H), 8.1 (d, 2 quinoline-H); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 11$, 57, 58, 59, 76, 121, 126, 128, 129, 130, 137, 138, 148, 162 ppm; ESI-MS: $m/z =$ calcd 372.42 ($M + H^+$), found 372.

(S)-3-(Benzylthio)-2-(bis(quinolin-2-ylmethyl)amino)propan-1-ol ((***S***)-**17a**, $C_{30}H_{29}N_3OS$)

Procedure B, yield 33.8%; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 2.4$ (dd, $J_1 = 6$ Hz, $J_2 = 10$ Hz, 1 S-CH_2), 2.8 (dd, $J_1 = J_2 = 9$ Hz, 1 S-CH_2), 3.3 (m, CH), 3.6 (t, $J = 14$ Hz, 1 CH_2O), 3.7 (s, Ph-CH_2-S), 3.8 (dd, $J_1 = 9$ Hz, $J = 6$ Hz, 1 CH_2O), 4.2 (d, $J = 9$ Hz, NCH_2), 7.25 (m, 2 Ph-H), 7.3 (m, 3 Ph-H), 7.5 (m, 2 quinoline-H), 7.7 (t, 4 quinoline-H), 7.8 (d, 2 quinoline-H), 8.1 (d, 2 quinoline-H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 30$, 38, 57, 62, 63, 122, 126.6, 127, 127.4, 127.6, 128, 129, 129.4, 130, 137, 138, 139, 148, 161 ppm; MALDI-TOF-MS: m/z = calcd 480.70 ($M + H^+$), found 480.17.

[(S)-2-(Bis(quinolin-2-ylmethyl)amino)-2-phenylethanol]copper(II) perchlorate
((***S***)-**14b**, $C_{28}H_{25}N_3O_9CuCl_2$)

ESI-MS: m/z = calcd 482.9 ($M + H^+$), found 483.

[(R)-2-(Bis(quinolin-2-ylmethyl)amino)-2-phenylethanol]copper(II) perchlorate
((***R***)-**14b**, $C_{28}H_{25}N_3O_9CuCl_2$)

ESI-MS: m/z = calcd 482.9 ($M + H^+$), found 483.

[(S)-2-(Bis(quinolin-2-ylmethyl)amino)-1-propanol]copper(II) perchlorate
((***S***)-**15b**, $C_{23}H_{23}N_3O_9CuCl_2$)

MALDI-TOF-MS: m/z = calcd 620.9 ($M + H^+$), found 622.1.

[(S)-1-Methoxy-N,N-bis(quinolin-2-ylmethyl)propan-2-amine]copper(II) perchlorate
((***S***)-**16b**, $C_{24}H_{25}N_3O_9CuCl_2$)

MALDI-TOF-MS: m/z = calcd 436.02 ($M + H^+$), found 435.32.

[(S)-3-(Benzylthio)-2-(bis(quinolin-2-ylmethyl)amino)propan-1-ol]copper(II) perchlorate
((***S***)-**17b**, $C_{30}H_{29}N_3O_9SCuCl_2$)

MALDI-TOF-MS: m/z = calcd 543.1 ($M + H^+$), found 543.

X-Ray Structures

CCDC 251037–251039 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cir, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

[(R)-2-(Bis(quinolin-2-ylmethyl)amino)-2-phenylethanol]acetonitrilocopper(II) perchlorate: A crystal (approximate dimensions $0.35 \times 0.22 \times 0.20$ mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker SMART system for a data collection at 173(2) K. 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 matrices determined from 130 reflections. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 30 s and a detector distance of 4.9 cm. A randomly oriented region of reciprocal space was surveyed to the extent of 1.5 hemispheres and to a resolution of 0.76 Å. Three major sections of frames were collected with 0.30° steps in ω at 3 different ϕ-settings and a detector position of $-28°$ in 2θ. The intensity data were corrected for absorption and decay (SADABS) [29]. Final cell constants were calculated from 3431

Table 2. Crystal data and structure refinement parameters

Formula	$C_{98}\ H_{95}\ Cl_{12}\ Cu_4\ N_{13}\ O_{26}$ (±)-([Cu(II)-(**9**, R=CH_3)])$_4$ $(ClO_4)_4 \cdot 2H_2O \cdot CH_3CN \cdot 4CH_2Cl_2$	$C_{30}\ H_{28}\ Cl_2\ Cu\ N_4\ O_9$ (R)-[Cu(**14**)-(CH_3CN)($ClO_4)_2$]	$C_{60}\ H_{54}\ B_2\ Cu_2\ F_8\ N_8\ O_2$ (R)-[(Cu(**14**))$_2$]($BF_4)_2$
Formula weight	2550.43	723.00	1219.81
Crystal system	Tetragonal	Orthorhombic	Monoclinic
Space Group	I-4	$P2_12_12_1$	$P2_1$
a/nm	1.9653(2)	1.16496(12)	1.3311(3)
b/nm	1.9653(2)	1.47683(16)	1.9314(4)
c/nm	1.3574(2)	1.74617(19)	2.2265(4)
α/°	90°	90°	90°
β/°	90°	90°	91.570(4)°
γ/°	90°	90°	90°
V/nm^3	5.2428(11)	3.0042(6)	5.7216(18)
Z	2	4	4
μ/mm^{-1}	1.188	0.968	0.820
Crystal size	$0.28\times0.15\times0.13$ mm^3	$0.35\times0.22\times0.20$ mm^3	$0.40\times0.16\times0.14$ mm^3
Reflections collected/unique	17263	25858	48093
R(int)	0.0521	0.0340	0.0557
Goodness-of-fit on F^2	1.011	1.036	1.034
$R1$ [$I>2\sigma(I)$], $wR2$	0.0423, 0.0937	0.0281, 0.0690	0.0617, 0.1378

strong reflections from the actual data collection after integration (SAINT 6.01, 1999) [30]. Refer to Table 2 for additional crystal and refinement information.

The structure was solved using SHELXS-86[3] and refined using SHELXL-97 [31]. The space group $P2_12_12_1$ was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided 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 unless stated otherwise. 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 $R1 = 0.0281$ and $wR2 = 0.0721$ (F^2, all data).

[(R)-2-(Bis(quinolin-2-ylmethyl)amino)-2-phenylethanol]copper(II) tetrafluoroborate: A crystal (approximate dimensions $0.40\times0.16\times0.14$ mm^3) was handled similarly; Table 2 describes crystal and refinement information. The final full matrix least squares refinement converged to $R1 = 0.0617$ and $wR2 = 0.1661$ (F^2, all data). The structure is quite clearly in space group $P2_1$ with $Z' = 2$, but has pseudo-glide symmetry that emulates space group $P2_1/n$. The (*S*)-isomer forces this structure to be noncentrosymmetric [33]. Both dications have approximate local two-fold symmetry. Along with the two stereoisomers there are four BF_4^- anions and four solvent molecules of acetonitrile. One phenyl group of the *B* molecule is sufficiently disordered that it required splitting into two equally populated parts. These carbon atoms were intentionally refined with isotropic displacement parameters. One BF_4^- anion was split into two equally populated parts. These atoms were refined with anisotropic displacement parameters with constraints between nearby atoms. The BF_4^- anions were restrained to being ideal tetrahedrons. All acetonitrile molecules were constrained to being linear with N–C = 1.136 Å and C–C = 1.470 Å. The anisotropic displacement parameters of the BF_4^- anions and the acetonitrile solvent molecules were restrained as independent rigid bodies. 595 restraints, plus 1 positional restraint as required by the $P2_1$ space group, were included in the refinement.

[Cu(II)-(**3**)]ClO_4: A crystal (approximate dimensions $0.28 \times 0.15 \times 0.13\,mm^3$) was examined similarly on a Bruker CCD area detector diffractometer. Refer to Table 2 for crystal and refinement information. The structure was solved using SIR92 [32] and refined using SHELXL-97 [31]. The structure contains a MeCN solvent molecule disordered over a -4 symmetry site. Most non-hydrogen atoms were refined with anisotropic displacement parameters. The nitrogen atom of a disorder MeCN molecule displayed poor anisotropic displacement parameters so was refined isotropically. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters except those of the disordered MeCN and water molecules. These hydrogen atoms were not included in the refinement but included in the final formula.

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