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Exploring the Scope of Redox-Triggered Chiroptical Switches: Syntheses, X-ray Structures, and Circular Dichroism of Cobalt and Nickel Complexes of *N,N*-Bis(arylmethyl)methionine Derivatives

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Dedicated to Professor Nina Berova on the occasion of her significant anniversary and her receiving the Chirality Medal 2007.

ABSTRACT *N,N*-Bis(arylmethyl)methionine derivatives are chiral ligands whose complexes with metal ions may show molecular helicity that can be modulated by defined structural processes. It was shown previously that exciton-coupled circular dichroism (ECCD) spectral amplitude could be modulated by one-electron copper redox chemistry in copper complexes of these ligands. Here we describe the further development of novel systems that show conformational changes resulting in the inversion of exciton chirality. The phenomenon was probed in a *N,N*-bis(arylmethyl)methionine derivative containing quinoline/pyridine moieties and a methionine carboxylate moiety. The sign of the ECCD of the complex formed between this ligand and $CoCl_2$ is negative, which suggests that the deprotonated carboxylate oxygen coordinates to the metal, but the sulfur atom does not. The sign of the ECCD inverts to positive upon addition of ascorbic acid, which can be turned back to negative upon further treatment with persulfate. X-ray quality crystals of three cobalt complexes and one nickel complex were obtained. The ascorbate-treated cobalt complex of the ligand and the same ligand with nickel, however, vary from the behavior expected from their X-ray crystal structures. It is clear that the solution and crystallographic structures of these complexes differ in several cases. *Chirality 20:585–591, 2008.* © 2008 Wiley-Liss, Inc.

KEY WORDS: exciton coupling; UV/vis spectroscopy; coordination chemistry; cobalt; nickel; copper; X-ray crystallography

INTRODUCTION

Chiroptical molecular switches attract substantial interest because of their stereochemical novelty and potential applications.[1,2] For example, such compounds have been used for absolute configurational assignment of organic compounds,[3] helical induction in liquid crystals,[4] molecular electronics applications,[5] and mechanical manipulation.[6] We are particularly interested in redox-triggered molecules whose molecular helicity can be modulated by defined structural processes.[3] Our approach to this problem grew out of our studies of conformationally biased, labile coordination complexes.[7] Central to these studies was the observation that tripodal ligands with a single chiral center in one of the arms experience a bias affording an additional element of helical chirality.[8] The propeller-like conformation adopted fixes the orientation of appended or inherent chromophores, 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.[11,12] 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.

It was found that methionine reacts with bromomethylquinoline to form ligands that complex Cu^{II} and show strong ECCD couplets.[13,14] The CD-active product is illustrated in Figure 1. 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 methylenes of the achiral arms, such

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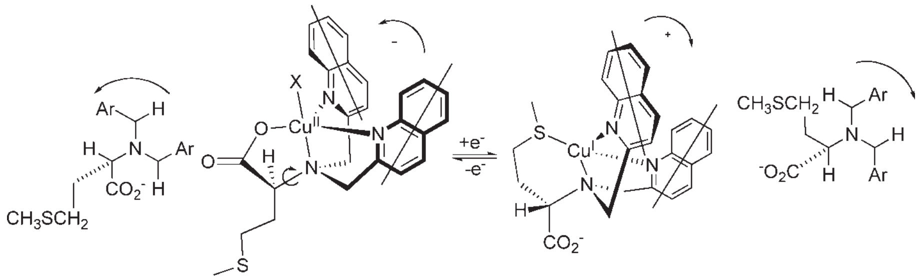

Fig. 1. *N,N*-Bis(2-quinolylmethyl)-L-methionine complexes with Cu^{II} and Cu^{I}. The chiral center of the amino acid dictates the orientation of the quinoline chromophores via a gearing mechanism as illustrated (Ar = 2-quinolyl or 2-pyridyl). The transition dipoles in the quinolines in the two complexes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

that a propeller forms from the planar carboxylate and quinoline groups (Fig. 1). The Cu^{I} complex gave a propeller complex with the opposite configuration because of the preference of Cu^{I} for coordination with the sulfur atom. 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 inverts the gearing, and therefore the orientation, of the quinoline moieties, leading to an ECCD couplet with the opposite sign. Synthetic and spectroscopic details plus further structural characterization of Zn^{II} and Cu^{II} complexes of (*S*)-*N,N*-bis(2-pyridylmethyl)-methionine ((*S*)-**1**) and its quinoline-containing analog (*S*)-*N,N*-bis(2-quinolylmethyl)methionine ((*S*)-**2**) have also been reported.[14] Crystal structures of Zn^{II} and Cu^{II} complexes showed that these metal ions coordinate with the carboxylate instead of the sulfide.[14] NMR spectra of the Cu^{I} complexes demonstrated Cu^{I}—S coordination. Other amino acid derivatives showed similar behavior with Cu^{I}, Cu^{II}, and Zn^{II}.[15,16]

In search of other metal ions that might exhibit interesting redox-dependent ligation modes with such ligands, we prepared several cobalt and nickel complexes and investigated their CD properties and their X-ray structures. Cobalt and nickel were selected because of the accessibility of other oxidation states. Given our reasoning that it is the softness of the Cu(I) in the known systems that drives the reorganization of the ligands, cobalt and nickel seemed to offer some potential to exhibit similar phenomena compared to other transition metal redox couples.

MATERIALS AND METHODS

All reagents and solvents were purchased from commercial sources and used as received, unless noted otherwise. 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 0.1 M *n*-Bu_4NPF_6 as supporting electrolyte in acetonitrile or methanol. FT-IR spectra (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 or a Bruker X-Flex MALDI-TOF using the matrix α-ACHC was used for mass spectrometry. Unless stated otherwise, UV–vis spectra were obtained on a Perkin-Elmer Lamda-5 instrument, and CD spectra (0.1 cm path length) were taken on an Aviv 212 CD instrument at ambient temperature in methanol. The synthesis of (*S*)-*N,N*-bis(2-pyridylmethyl)methionine ((*S*)-**1**) and (*S*)-*N,N*-bis(2-quinolylmethyl)methionine ((*S*)-**2**) were reported elsewhere.[14] The optical rotation of these ligands was determined as follows: (*S*)-**1**, $[\alpha]_D^{21} = -19°$ (*c* 0.086, 4:1 acetonitrile:water) and (*S*)-**2**, $[\alpha]_D^{21} = -75°$(*c* 0.0049, methanol).

[Co^{II}(1)]ClO$_4$

Caution! *Perchlorate salts of metal complexes with organic ligands are potentially explosive. They should be handled in small quantities and with caution.* This compound was prepared by precipitation from methanol in a manner similar to $[Zn(\mathbf{1})]ClO_4$.[14] To a methanolic solution of $Co(ClO_4)_2{\cdot}6H_2O$ (55.3 mg, 0.151 mmol in 10 ml methanol) was added a solution of (*S*)-(*l*)-**1** (49.9 mg, 0.151 mmol in 10 ml methanol) and stirred for 30 min. The resultant precipitate was filtered under suction and dried under vacuum to yield 58.4 mg (80%) of the complex, which was green in color. Crystals suitable for X-ray diffraction studies were obtained from methanol/water by slow evaporation over several days. The crystallographic structure obtained was for racemic material, and it was found that the crystals showed no optical activity. Anal. Calcd for $C_{17}H_{20}N_3O_6SCoCl$: C, 41.77; H, 4.12; N, 8.60. Found: C, 42.00; H, 4.02; N, 8.74. FT-IR (cm^{-1}): 1608 (CO); 1556 (CoN); 1099 (ClO_4). MS (*m/e*): 389 $(CoL)^+$, mp 250°.

[Co^{II}(2)Cl]

To a methanolic solution of $CoCl_2{\cdot}6H_2O$ (179 mg, 0.75 mmol in 6 ml of methanol) was added a solution of (*S*)-**2** (220 mg, 0.51 mmol in 6 ml methanol) and stirred for 2 h at 50°C. A greenish-blue precipitate was filtered under suction and dried under vacuum to yield 174 mg (65%) of the complex. Crystals suitable for X-ray diffraction studies were obtained from methanol/water by slow evaporation. Anal. Calcd for $C_{25}H_{24}N_3O_2SCoCl{+}HCl$: C, 53.49; H, 4.49; N, 7.49. Found: C, 53.76; H, 4.56; N, 7.65. FT-IR (cm^{-1}):

TABLE 1. Crystal data and structure refinement

	Complex			
	(±)-$Co^{II}(\mathbf{1})ClO_4$	$Co^{II}((S)\text{-}\mathbf{2})Cl$	$Co_2^{II}((S)\text{-}\mathbf{2})_2(C_2O_4)$	$[Ni_4^{II}((S)\text{-}\mathbf{2})_4](ClO_4)_4$
Empirical formula	$C_{17}H_{20}ClCoN_3O_6S$	$C_{52}H_{48}Cl_2Co_2D_8N_6O_6S_2$	$C_{26}H_{24}CoN_3O_4S$	$C_{104}H_{102}Cl_4N_{14}Ni_4O_{24}S_4$
Formula weight	488.80	1121.96	533.47	2436.88
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Tetragonal	Monoclinic
Space group	$P2(1)/n$	$P2(1)$	$P4_12_12$	$P21$
a (Å)	9.493(2)	6.924(1)	14.656(1)	14.397(2)
b (Å)	9.327(2)	28.835(5)	14.656(1)	15.650(2)
c (Å)	24.008(5)	13.517(2)	31.999(4)	23.871(3)
α (°)	90	90	90	90
β (°)	100.859(3)	90.013(3)	90	98.881(3)
γ (°)	90	90	90	90
Volume (Å^3)	2087.6(7)	2698.7(8)	6873(1)	5314.0(12)
Z	4	2	8	2
Density (calculated) (mg/m^3)	1.555	1.381	1.031	1.523
Absorption coefficient (mm^{-1})	1.089	0.844	0.587	0.957
F(000)	1004	1156	2208	2520
Crystal habit and color	green, block	violet, needle	orange, block	blue, block
Crystal size (mm^3)	0.21 × 0.20 × 0.18	0.31 × 0.13 × 0.07	0.28 × 0.13 × 0.13	0.28 × 0.24 × 0.20
Theta range for data collection	1.73–25.06°.	0.71–27.53°.	1.53–25.09°	1.55–25.06°
Reflections collected	12,629	24,206	23,853	35,882
Independent reflections	3699	11,552	6102	18,496
Observed reflections	3168	10,946	3166	14,295
Completeness to theta = 25.06°	99.8%	99.3%	99.7%	99.6%
Data/restraints/ parameters	3699/106/313	11,552/5/638	6102/2/300	18,496/71/1464
GOF	1.036	1.008	1.012	1.058
$R1,wR2[I > 2\text{sigma}(I)]$	0.0536, 0.1253	0.0502, 0.1347	0.0847, 0.2149	0.0583, 0.1312
R indices (all data)	0.0648, 0.1306	0.0529, 0.1363	0.1377, 0.2360	0.0844, 0.1447
Flack parameter		0.047(18)	0.17(4)	0.022(13)

1617 (CO); 1504 (CoN). MS (m/e): 489.2 $(CoL)^+$, mp 189°, $[\alpha]_D^{21} = -236°$ (c 0.058, methanol).

[Ni(2)]ClO$_4$

To a methanolic solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (275 mg, 0.75 mmol in 6 ml of methanol) was added a solution of (S)-**2** (220 mg, 0.51 mmol in 6 ml methanol) and stirred for 2 h at 50°C. A greenish precipitate was filtered under suction and dried under vacuum to yield 207 mg (69%) of the complex. Crystals suitable for X-ray diffraction studies were obtained from methanol/water by slow evaporation. Anal. Calcd for $C_{25}H_{24}N_3O_2SCoCl_2 \cdot CH_3OH \cdot H_2O$: C, 48.90; H, 4.54; N, 6.70. Found: C, 48.85; H, 4.60; N, 6.58. MS (m/e): 489 $(NiL)^+$, $[\alpha]_D^{21} = -46°$ (c 0.062, methanol).

X-ray Crystallographic Analysis

A very small crystal was placed onto the tip of a 0.1-mm diameter glass capillary and mounted on a Bruker SMART Platform CCD diffractometer 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 various numbers of reflections. The data collection was carried out using Mo Kα radiation (graphite monochromator). A randomly oriented region of reciprocal space was surveyed to the extent of 1.5 hemispheres and to a resolution of 0.84 Å. Four major sections of frames were collected with 0.30° steps in ω at four different ϕ settings and a detector position of −28° in 2θ. The intensity data were corrected for absorption and decay (SADABS).[17] Please refer to Table 1 for additional crystal and refinement information. Unless otherwise noted, the structures were solved using SHELXS-86[18] or SHELXS-97[19] and refined using SHELXL-97.[19] A direct-methods solution was calculated, which provided most nonhydrogen atoms from the E-map. Full-matrix least squares/difference Fourier cycles were performed which located the remaining nonhydrogen atoms. All nonhydrogen 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.

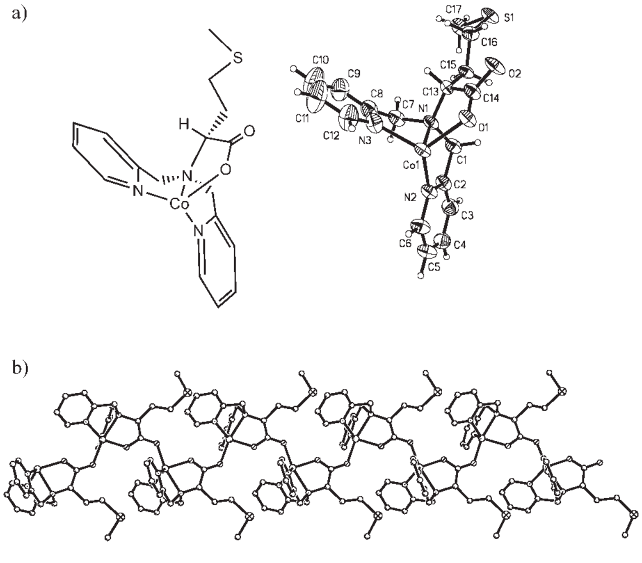

Fig. 2. (**a**) ORTEP view of the cation portion of the complex Co^{II}(**1**)-ClO$_4$. Atom O2′ from an adjacent complex is excluded for clarity. (**b**) Helical chain formed by bridging carboxylate groups in the solid state. One enantiomer is shown here, but crystallographic structure is of the racemate.

RESULTS AND DISCUSSION

The coordination chemistry of these ligands was explored with cobalt and nickel salts because of the accessibility of oxidation states that might give ligand reorganization. Generally, the metal salts were reacted with the ligands to produce complexes that gave precipitates that were characterized by elemental analysis. Some of the complexes were then reacted with ascorbic acid as a reductant, which had previously worked well in the reduction of Cu(II) to produce Cu(I) complexes.[13,20]

Co^{II}(1)ClO$_4$

This complex was prepared by precipitation. The structure is analogous to the structures of recently published of Zn^{II} and Cu^{II} complexes of ligand **1**.[14] An ORTEP[21] view of the complex is shown in Figure 2. In this structure, Co^{II} is five-coordinated and possesses a trigonal bipyramidal geometry. The ligand **1** 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 Co^{II} 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 cobalt-oxygen bond distances are very similar; that for Co—O1 is 2.010(3) Å, and that for Co—O2 (from an adjacent ligand) is 1.999(3) Å. The branch containing the sulfur atom, which is not coordinated to the metal ion, is modeled as disordered over two positions (76:24). The perchlorate counter ion is modeled as disordered over three positions (83:8:9). As with the Cu(**1**) and Zn(**1**) complexes, the complex forms a one-dimensional polymer in the solid state resulting from bridging of carboxylate groups (Fig. 2b). Such aggregates dissociate in the polar solvent used for solution measurements. The 1D polymer has a supramolecular helical structure. Interestingly, the crystal is racemic, with racemization having occurred during the slow crystallization process.

Co^{II}(2)Cl

An ORTEP view of the complex is shown in Figure 3. The space group was determined to be $P2_1$. The structure is a pseudomerohedral twin with a twin index of 1. Although the crystal system is monoclinic based on the data, the β angle is 90.013(3)°, which allows for the cell to transform to the orthorhombic system via a rotation about the *a*-axis. The ratio of the main to the twinned component is 59:41 by mass. The structure was also tested for inversion twinning, but nothing significant was found.

In this structure, Co^{II} is five-coordinated and possesses a trigonal bipyramidal geometry. The ligand (*S*)-**2** coordinates to the metal through two quinoline nitrogens, the tertiary amine nitrogen and the deprotonated carboxylate oxygen atoms and the chloride. Two quinoline nitrogens and one carboxylate oxygen form the trigonal plane with the central Co^{II} atom, while a tertiary amino nitrogen and the chloride occupy the apical positions. The sulfur atom does not coordinate the cobalt. There is only one chloride per cobalt in the crystal, consistent with a Co^{II} oxidation state. The asymmetric unit consists of two independent cobalt molecules and two deuterated methanol molecules, one of which is disordered over two positions (76:24). Per unit cell, there is also a solvent channel parallel to the *a*-axis (Fig. 3b) of 206 Å^3 which accounts for 78 electrons, as calculated by program PLATON, function SQUEEZE.[22,23] However, the largest residual peak is only 1.2 electrons per Å^3, suggesting either extreme disorder or that the solvent can escape readily via the channel. Also noteworthy is that while this structure forms channels, the previous structure forms chains.

Co$_2^{II}$(2)$_2$(C$_2$O$_4$)

This complex was prepared from [Co^{II}(**2**)Cl] by reaction with ascorbic acid. The structure shows the presence of an oxalate dianion bridging two cobalt atoms. Oxalate is an oxidation product of ascorbic acid.[24,25] An ORTEP view of the complex is shown in Figure 4. The space group $P4_12_12$ was determined based on systematic absences and intensity statistics. The structure solution refines as an inversion twin in a ratio of 83:17, indicating that partial racemization occurred under the conditions of crystallization. One half of the oxalate-bridged dimer is unique, with the other half being generated by a twofold axis which runs along C1 and C2. The end of the sulfur branch is modeled as disordered over two positions (50:50). Highly disordered solvent was detected which could not be modeled. The data were corrected to remove this electron density using program PLATON, function SQUEEZE,[23] which determined that there were 827 electrons in 2697 Å^3 per unit cell. The tremendous amount of solvent may also explain the large thermal ellipsoids, since the molecules were in a "loose" crystalline lattice, thus allowing more movement than expected for a data collection at 173 K. Constraints (AFIX 66) were used on the phenyl rings (C7–C12,

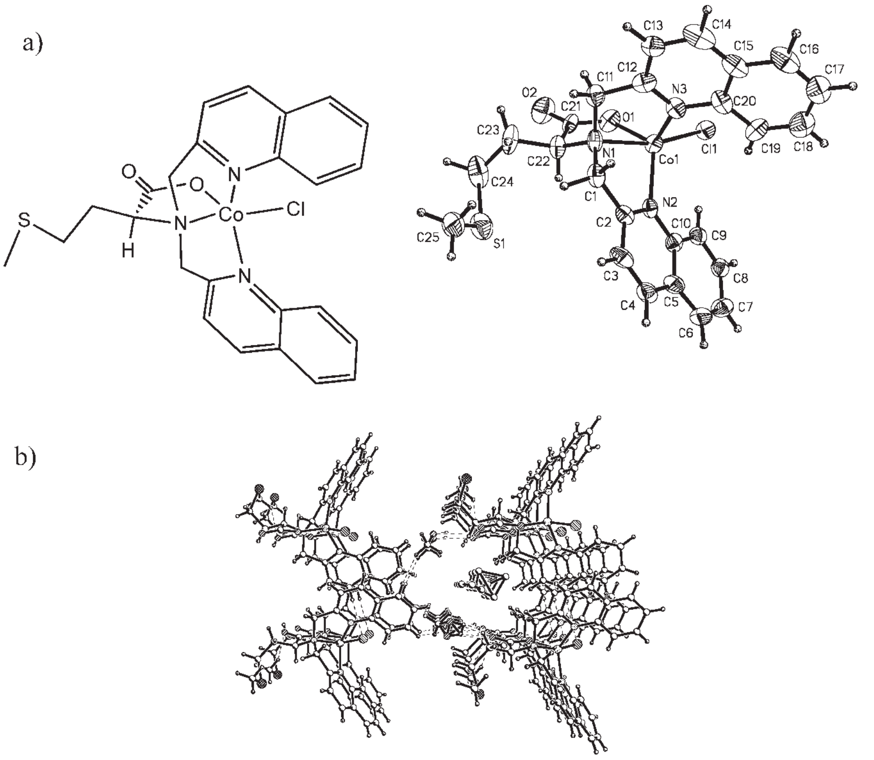

Fig. 3. (**a**) ORTEP view of the complex $Co^{II}(\mathbf{2})Cl$. (**b**) Solvent channel parallel to the *a*-axis in the crystal of $Co^{II}(\mathbf{2})Cl$.

C17–C22) to make them ideal. It must be noted that, because of the use of function SQUEEZE, various fields in Table 1 (empirical formula, formula weight, *F*(000), etc.) are incorrect. In this structure, Co^{II} is six-coordinated and possesses octahedral geometry. Ligand **2** coordinates to the metal through two quinoline nitrogens, the tertiary amine nitrogen and the deprotonated carboxylate oxygen from the parent-amino acid moiety and two other oxygen atoms from the oxalate (the deprotonated oxygen on one carbon and the carbonyl oxygen on the other carbon from the oxalate). The other two oxygen atoms coordinate another cobalt that is ligated to another molecule of (*S*)-**2** to form a dimer. The sulfur atoms do not coordinate to the metal ions.

$[Ni_4^{II}(2)_4](ClO_4)_4$

An ORTEP view of the complex is shown in Figure 5. The structure was solved using SIR923 and refined using SHELXL-97. There are also four ClO_4^- and two MeCN molecules per main molecule. The structure is a tetranuclear aggregate of four metal ions and four ligands. In this structure, Ni^{II} is six-coordinated and possesses octahedral geometry. The ligand (*S*)-**2** coordinates to the metal through two quinoline nitrogens, the tertiary amine nitrogen and the deprotonated carboxylate oxygen from the parent-amino acid moiety and two other oxygen atoms from the carboxylate of a second (*S*)-**2**. The two oxygen atoms from the carboxylate of the first ligand coordinate to a second nickel.

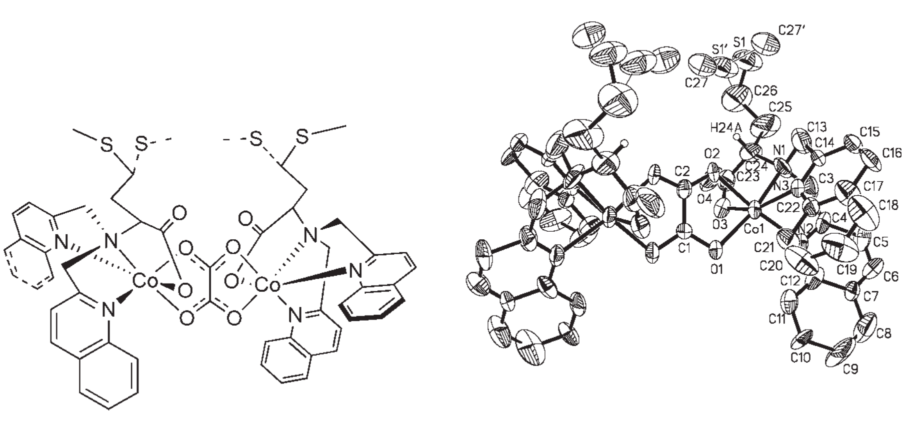

Fig. 4. ORTEP view of the complex $Co_2^{II}((L)\text{-}\mathbf{2})_2(C_2O_4)$. There is one crystallographic unique Co(**2**) unit and a second, present by symmetry, included in this diagram. The disorder of the thiomethyl moiety is also depicted.

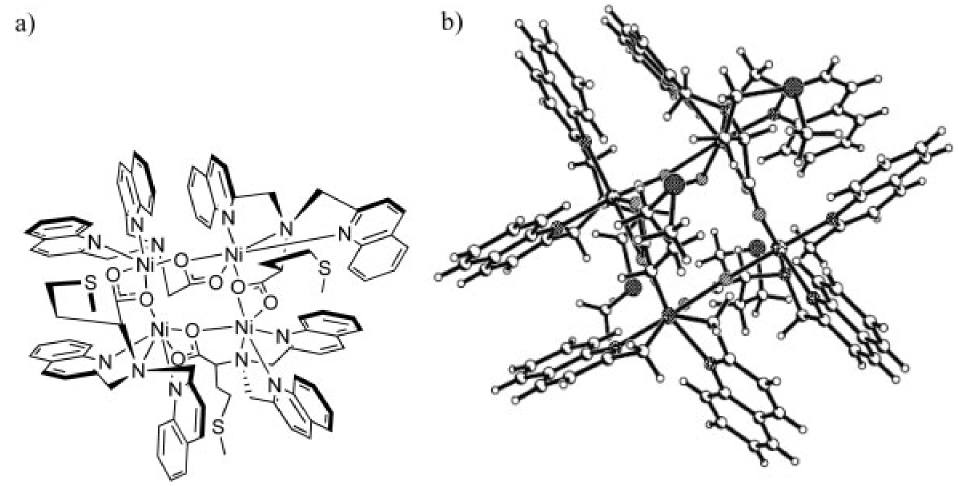

Fig. 5. (**a**) View of the cation portion of the complex $[Ni_4^{II}(\mathbf{2})_4](ClO_4)_4$. (**b**) ORTEP view of the Ni atoms and atoms within their inner coordination sphere.

The nickel cationic unit is quadrupled via carboxylate-oxygens linkages. The sulfur atoms do not coordinate to the metal ions.

UV and CD Studies

The UV spectra of the quinoline-containing compound (*S*)-**2** and Cu^{II}, Cu^{I}, and Zn^{II} complexes were reported previously,[14] and the peaks in their absorption bands were assigned. Upon addition of $CoCl_2$ to this ligand, the ^1B_b bands of the quinoline moieties blueshift slightly by 4 nm with a $\lambda_{max} = 231$ nm. Addition of ascorbic acid has a very small effect on this band ($\lambda_{max} = 230$ nm). Subsequent treatment with ammonium persulfate reverts the miniscule change ($\lambda_{max} = 230$; Fig. 6). Generally, the UV–vis spectra shown here exhibit the same properties as the related Cu^{II} and Zn^{II} compounds, which have been discussed in detail. The free ligand (*S*)-**2** exhibited almost no CD signal. Addition of $CoCl_2$ resulted in intense CD signals which display nonconservative ECCD spectra (Fig. 6). Elemental analysis showed that the complex formed is the HCl adduct of $Co(\mathbf{2})Cl$, although the elemental analysis could also be interpreted as the $Co^{III}(\mathbf{2})Cl_2$ complex, but the preponderance of other data, including X-ray crystallography, indicated that it must be the HCl salt of a Co^{II} complex . The sign of the ECCD of this complex is negative, similar to the Cu^{II} and Zn^{II} complexes of (***S***)-**2**.[14] The sign of the ECCD inverted to positive upon addition of ascorbic acid, and was turned back to negative upon further treatment with ammonium persulfate. Sodium thiosulfate was also used successfully as reductant, and gave more reproducible results than ascorbate. This behavior is consistent with a structural hypothesis in which the original complex formed by addition of $CoCl_2$ to (***S***)-**2** is a Co^{II} complex. Addition of reductant might result in a reduced cobalt (Co^{I}) species,[26–28] but may also yield a transient intermediate such as an adduct with the reductant or a byproduct. Addition of oxidant would then return either transient reduced species to the Co^{II} oxidation state.

The complexes formed by mixing (***S***)-**2** and $Ni(ClO_4)_2$ exhibit ECCD with a positive sign as is shown in Figure 7, which is opposite to that expected if the carboxylate were coordinated to the metal. However, the crystallographic structure of $Ni((S)\text{-}\mathbf{2})ClO_4$ shows a carboxylate-coordinated tetramer with the ligand in two different conformations. In one conformation, the quinolines show a very small dihedral angle and would therefore be expected to give only a weak contribution to the ECCD spectrum. In the other ligand conformation, the quinoline moieties are oriented in a negative chiral sense, which would be expected to give a negative ECCD couplet. It is possible that the ECCD spectrum may derive from interaction between quinolines from different ligands within this aggregated structure. However, both positive and negative relative pairwise quinoline orientations can be identified in the crystal structure, and so there is no obvious prediction that can be made regarding the ECCD sign of the couplet. Additionally, such aggregates often dissociate into other species in solution,[14] further complicating the analysis.

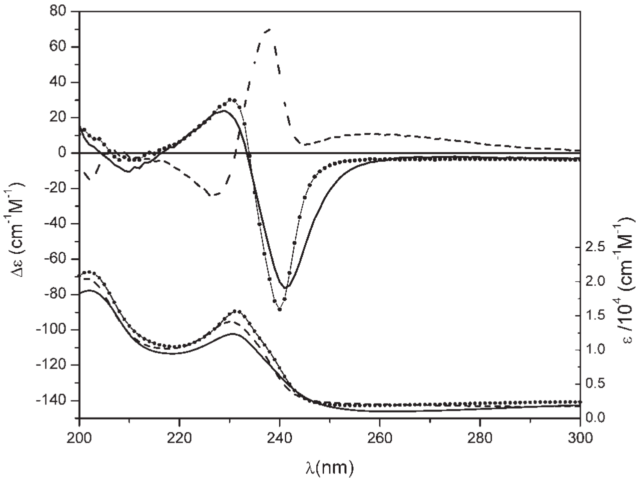

Fig. 6. UV (bottom) and CD (top) spectra of $[Co^{II}(\mathbf{2})Cl]$ itself (solid curve) in methanol ($c = 0.1$ mM), after it was treated with 1 equiv of ascorbic acid (dash curve) and after the previous mixture was subsequently treated with 1 equiv of ammonium persulfate (dot-on-line curve).

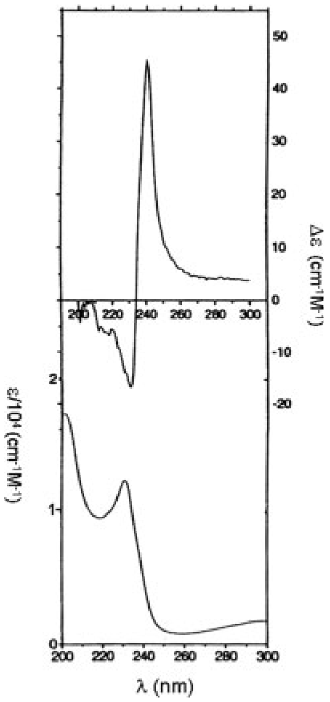

Fig. 7. UV (bottom) and CD (top) spectra of [Ni(**2**)]ClO_4 in methanol (c = 0.1 mM).

CONCLUSIONS

This report describes the further 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. Previous work with Zn^{II}, Cu^{II}, and Cu^{I} yielded a consistent picture of the conformational properties and redox-induced ligand reorganization in this system. Certain Co(II) complexes showed similar behavior to the previously studied copper complexes and gave inversion of chirality when reacted with reducing agents, but Ni(II) complexes did not show the expected CD spectra. It is clear that the solution and crystallographic structures of these complexes differ in several cases.

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