Inorg. Chem. **2005**, *44*, 2585–2587

Inorganic Chemistry
Communication

Self-Assembly of a Fluorescent Chiral Zinc(II) Complex That Leads to Supramolecular Helices

Maddela Prabhakar, Panthapally S. Zacharias,* and Samar K. Das*

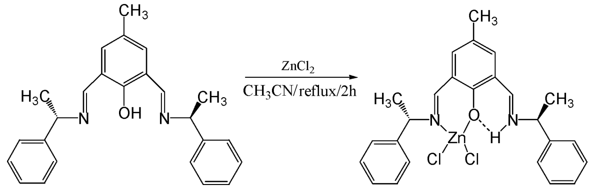
School of Chemistry, University of Hyderabad, Hyderabad 500046, India

Received December 16, 2004

The chiral Zn(II) complex [ZnLCl$_2$], **1** {L = 4-methyl-2,6-di[(*S*)-(+)-1-phenylethyliminomethyl] phenol}, self-assembles via C–H···Cl hydrogen bonding into supramolecular helices. Complex **1** exhibits emission in solution at room temperature in the visible range. Crystal data for **1**: orthorhombic space group $P2_12_12_1$, $a = 9.614(2)$ Å, $b = 13.825(3)$ Å, $c = 18.667(3)$ Å, $V = 2481.1(8)$ Å^3, $Z = 4$.

There has been considerable interest in helical supramolecular architectures, particularly helices from coordination compounds.[1] In most of these helical structures, the building units (e.g., coordination compounds) are linked via covalent bonds.[2] Even though supramolecular architecture has largely taken advantage of noncovalent (e.g., hydrogen-bonding) interactions,[3] hydrogen-bonded assemblies of coordination compounds that lead to helical structures have not been explored much. We report here a supramolecular left-handed helix, formed by C–H···Cl hydrogen-bonding interactions, using the chiral Zn(II) complex [ZnLCl$_2$], **1** {L = 4-methyl-2,6-di[(*S*)-(+)-1-phenylethyliminomethyl] phenol}, as the building unit. As expected, compound **1** exhibits both chirality and emissive properties. Coordination compounds that give both circular dichroism and emission signals at room temperature are well documented in literature.[4]

Scheme 1



The enantiopure ligand L (Scheme 1) is prepared in a Schiff-base condensation reaction of 1 equiv of 2,6-diformyl-4-methyl phenol with 2 equiv of (*S*)-(−)-1-phenylethylamine in acetonitrile. Reaction of zinc(II) chloride and optically pure ligand L afforded the neutral complex [Zn^{II}LCl$_2$] (**1**) in good yield (Scheme 1).[5]

The crystals of [ZnLCl$_2$] (**1**) were characterized by elemental and spectral analyses[6] including single-crystal X-ray structure determination.[7] The molecular structure of the Zn(II) complex **1** is presented in Figure 1. The zinc atom in **1** is four-coordinated with N(1), an O(1) donor (from the ligand L), and two chloride ligands in a distorted tetrahedral geometry. The chiral ligand L [chiral centers are C(18) and

---

* To whom correspondence should be addressed. Fax: (+91) 40 2301 2460 (S.K.D.). Tel.: (+91) 40 2301 1007 (S.K.D.). E-mail: skdsc@uohyd.ernet.in (S.K.D.).

(1) (a) Abrahams, B. F.; Batten, S. R.; Hamit, H.; Hoskins, B. F.; Robson, R. *J. Chem. Soc., Chem. Commun*. **1996**, 1313. (b) Piguet, C.; Bernardinelli, G.; Hopfgartner, G. *Chem. Rev.* **1997**, *97*, 2005. (c) Aspinall, H. C.; Bickley, J. F.; Dwyer, J. L. M.; Greeves, N.; Steiner, A. *Angew. Chem., Int. Ed*. **2000**, *39*, 2858.

(2) (a) Erxleben, A. *Inorg. Chem*. **2001**, *40*, 412. (b) Nomiya, K.; Takahashi, S.; Noguchi, R. *J. Chem. Soc., Dalton Trans.* **2000**, 1343. (c) Niklas, N.; Hampel, F.; Alsfasser, R. *J. Chem. Soc., Chem. Commun*. **2003**, 1586. (d) Withersby, M. A.; Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W.-S.; Schroeder, M. *Angew. Chem., Int. Ed.* **1997**, *36*, 2327. (e) Whang, D.; Heo, J.; Kim, C.-A.; Kim, K. *J. Chem. Soc., Chem. Commun*. **1997**, 2361. (f) Ranford, J. D.; Vittal, J. J.; Wu, D.; Yang, X. *Angew. Chem., Int. Ed.* **1999**, *38*, 3498. (g) Ezuhara, T.; Endo, K.; Aoyama, Y. *J. Am. Chem. Soc.* **1999**, *121*, 3279. (h) Ellis, W. E.; Schmitz, M.; Arif, A. A.; Stang, P. J. *Inorg. Chem*. **2000**, *39*, 2547. (i) Siemeling, U.; Scheppelmann, I.; Neumann, B.; Stammler, A.; Stammler, H.-G.; Frelek, J. *J. Chem. Soc., Chem. Commun*. **2003**, 2236.

(3) For example, see: Hanessian, S.; Gomtsyan, A.; Simard, M.; Roelens, S. *J. Am. Chem. Soc*. **1994**, *116*, 4495.

(4) (a) Barron, J. A.; Glazier, S.; Bernhard, S.; Takada, K.; Houston, P. L.; Abruna, H. D. *Inorg. Chem.* **2003**, *42*, 1448. (b) Bilakhiya, A. K.; Tyagi, B.; Paul, P.; Natarajan, P. *Inorg. Chem.* **2002**, *41*, 3830. (c) Canary, J. W.; Allen, C. S.; Castagnetto, J. M.; Wang, Y. *J. Am. Chem. Soc*. **1995**, *117*, 8484. (d) Castagnetto, J. M.; Canary, J. W. *J. Chem. Soc., Chem. Commun.* **1998**, 203. (e) Ziegler, M.; von Zelewsky, A. *Coord. Chem. Rev.* **1998**, *177*, 257. (f) Browne, W. R.; Hesek, D.; Gallagher, J. F.; O'Connor, C. M.; Killeen, J. S.; Aoki, F.; Ishida, H.; Inoue, Y.; Villani, C.; Vos, J. G. *J. Chem. Soc., Dalton Trans.* **2003**, 2597. (g) Browne, W. R.; O'Connor, C. M.; Villani, C.; Vos, J. G. *Inorg. Chem.* **2001**, *40*, 5461. (h) Fletcher, N. C.; Keene, F. R.; Viebrock, H.; von Zelewsky, A. *Inorg. Chem.* **1997**, *36*, 1113.

(5) Synthesis of [ZnLCl$_2$] (**1**): To a solution of 2,6-diformyl-4-methylphenol (2.46 g, 15 mmol) in 40 mL of acetonitrile was added (*S*)-(−)-1-phenylethylamine (3.63 g, 30 mmol) in 10 mL of acetonitrlile. The reaction mixture was refluxed for 4 h. To the resulting Schiff base, formed in situ, was added anhydrous ZnCl$_2$ (2.04 g, 15 mmol), and the mixture was refluxed for another 2 h. It was then filtered, and the filtrate was kept in an open conical flask at room temperature for 1 week, yielding 5.62 g of pale yellow crystals of **1** (74%).

(6) Spectral data for **1**: Optical rotation $[\alpha]_D^{25} = +86$ (c 1, ethanol). CD λ_{max} ($\Delta\epsilon$) (CH$_3$CN): 411 (+24.79), 302 (+0.51), 256 (+52.71), 217 (−123.74). ^{1}H NMR (CDCl$_3$) δ: 1.76 (d, 3H, $J = 6.82$ Hz, CH$_3$), 2.06 (d, 3H, $J = 6.82$ Hz, CH$_3$), 2.13 (s, 3H, Ar–CH$_3$), 4.58 (q, 2H, $J = 6.84$ Hz, CH), 7.16–7.48 (m, 12H, Ar–CH), 7.97 (s, 1H, HC=N), 8.18 (s, 1H, HC=N). IR ν_{max} (cm^{-1}): 1660, 1628, 1547. Anal. Calcd for C$_{25}$H$_{26}$N$_2$OZnCl$_2$ (M_w = 506.78 g mol^{-1}): C 59.25, H 5.17, N 5.53%. Found: C 59.26, H 5.24, N 5.47%. UV–vis (CH$_3$CN) [λ_{max}/nm (ϵ/M^{-1}cm^{-1})]: 414 (4400), 353 (6700), 243 (34 500).

10.1021/ic048236h CCC: $30.25

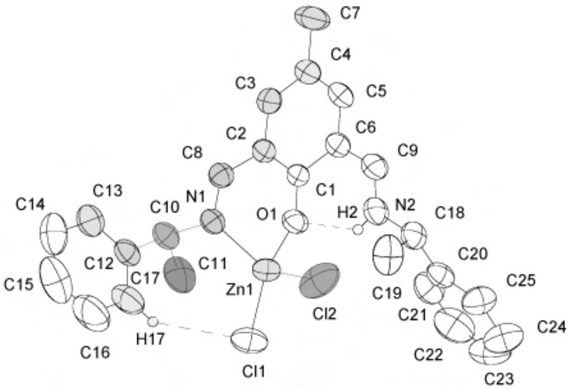


Figure 1. Thermal ellipsoid plot of the structure of **1**. Hydrogen atoms have been omitted for clarity (hydrogen atoms involved in the intramolecular hydrogen-bonding interactions are shown). C(18) and C(10) are chiral centers.

C(10)] has two arms with two donor nitrogen atoms. One nitrogen [N(1)] of one arm is coordinated to zinc, and the nitrogen [N(2)] of the other arm remains uncoordinated. This is due to the fact that phenolic hydroxyl [O(1)] gets deprotonated and N(2) gets protonated during complexation (Figure 1). This is also evidenced in the IR spectrum of the complex, in which the hydroxyl stretching of the free ligand L at ~3400 cm^{-1} is not observed. This kind of proton transfer is known in the current literature.[8] There are two intramolecular hydrogen bonds: N(2)−H(2)···O(1) [2.615(5) Å] and C(17)−H(17)···Cl(1) [3.533(7) Å]. Complex **1** self-assembles via hydrogen bonding into supramolecular helices. It is the C(13)−H(13)···Cl(2) intermolecular hydrogen bond [3.665(6) Å in length] that drives the formation of the helix as shown in Figure 2. A systematic investigation of C−H···Cl hydrogen-bonding interactions, using inorganic supramolecular synthons, has recently been reported.[9] The hydrogen-bonding parameters of the C−H···Cl bond (present work) are quite comparable to those of C−H···Cl bonds in other reported systems.[9,10] The path of the helix (Figure 2) can be traced by following the hydrogen bonds counterclockwise around the 2-fold screw axis of the helix. At the molecular level, the crystal contains a single enantiomer of the complex **1**. This local chirality translates throughout the crystal into the formation of only left-handed helices at the supramolecular level (Figure 2). Three zinc complex fragments form one helix turn in **1** with a pitch of 13.825 Å. The absolute configuration of the compound molecule was successfully determined by refining the Flack parameter [0.017(19)].[11]

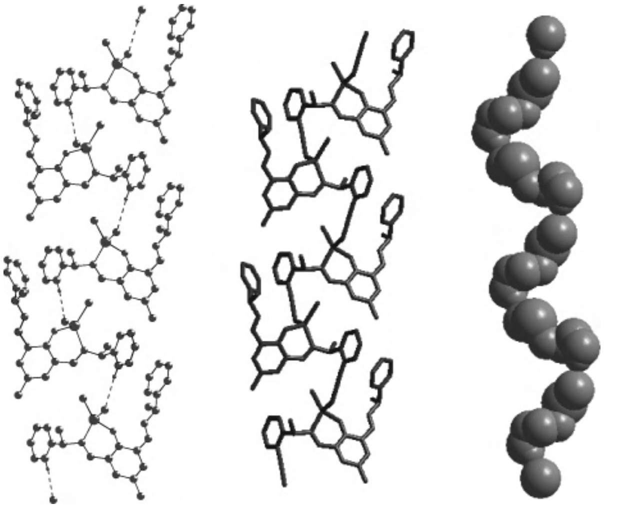


Figure 2. View illustrating intermolecular C−H···Cl hydrogen-bonding interactions between adjacent molecules that lead to the formation of hydrogen-bonded helices. All hydrogen atoms except those involved in hydrogen bonding have been omitted for clarity. Left, ball-and-stick presentation; center, wire-frame presentation; and right, space-filling plot (helical backbone).

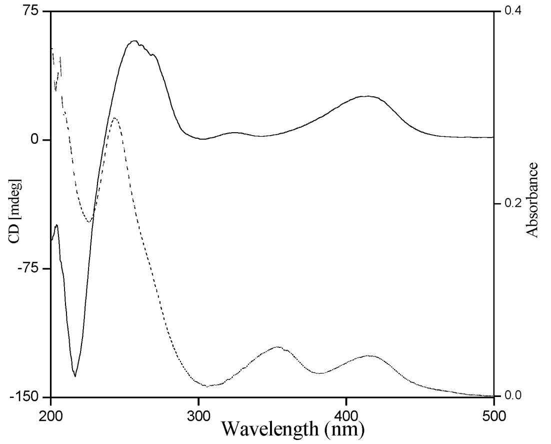


Figure 3. Circular dichroism (solid line) and electronic (dashed line) spectra of **1** in 1 × 10^{-5} M MeCN solution.

The optical activity of Zn complex **1** is induced by the chiral ligand L.[12] The UV−visible spectrum of zinc complex **1** is characterized by an intense band at 243 nm and two peaks at 353 and 414 nm, as shown in Figure 3. The circular dichroism (CD) spectrum of the synthesized chiral ligand L shows positive bands at around 350 and 245 nm. As expected, the CD spectrum of **1** exhibits positive bands (Figure 3).

The fluorescence properties of L and [ZnLCl$_2$] (**1**) were studied in MeCN solutions. The experiment reveals that the Zn^{2+} ion enhances the fluorescence. The fluorescence spectra of L and [ZnLCl$_2$] (**1**) are shown in Figure 4. There is a significant band shift and increase in fluorescence intensity for [ZnLCl$_2$] (**1**). The maximum excitation of the zinc complex is at 414 nm, and the maximum emission is at 504 nm. The fluorescence intensity at 504 nm is ca. 12 times of that of the ligand at 580 nm (Figure 4).

---

(7) Crystal data for **1**: $C_{25}H_{26}N_2Cl_2OZn$, M_w = 506.75, pale yellow prism, crystal dimensions 0.62 × 0.60 × 0.60 mm, orthorhombic, $P2_12_12_1$, a = 9.614(2) Å, b = 13.825(3) Å, c = 18.667(3) Å, V = 2481.1(8) Å^3, Z = 4, μ(Mo Kα) = 1.224 mm^{-1}, T = 293(2) K; 3197 reflections measured, direct methods with SHELXS-97 and refinement on F^2 using SHELXL-97. R1 = 0.0352 and wR2 = 0.0743.

(8) Pizzala, H.; Carles, M.; Stone, W. E. E.; Thevand, A. *J. Chem. Soc., Perkin Trans. 2* **2000**, 935.

(9) Balamurugan, V.; Hundal, M. S.; Mukherjee, R. *Chem. Eur. J.* **2004**, *10*, 1683.

(10) (a) Xuan, R.; Hu, W.; Yang, Z.; Xuan, R. *Acta Crystallogr.* **2003**, *C59*, m112. (b) Vembu, N.; Nallu, M.; Garrison, J.; Youngs, W. J. *Acta Crystallogr.* **2003**, *E59*, o939. (c) Braga, D.; Draper, S. M.; Champeil, E.; Grepioni, F. *J. Organomet. Chem.* **1999**, *573*, 73.

(11) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.

(12) von Zelewsky, A.; Mamula, O. *J. Chem. Soc., Dalton Trans.* **2000**, 219.

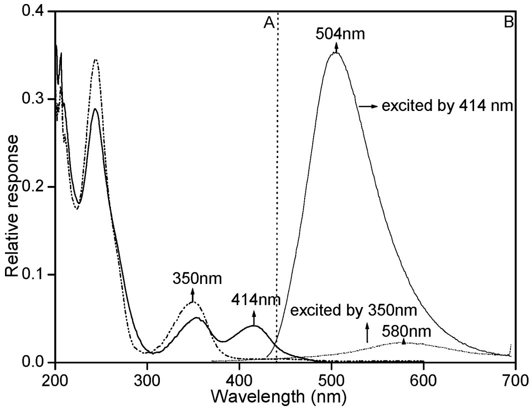


Figure 4. Fluorescence spectra of L and **1** at 298 K in 1×10^{-5} M MeCN solution (left halves are excitation spectra and right halves are emission spectra). The dashed line corresponds to ligand L and the solid line to zinc complex **1**.

The emission band (at 580 nm) of the free ligand L does not shift with varying concentration in MeCN solutions. On the other hand, the emission band of [ZnLCl$_2$] (**1**) is concentration-dependent: the band maxima gradually shifts to lower energy with increasing concentrations (see Supporting Information). This shift could be due to the intermolecular hydrogen-bonding association of [ZnLCl$_2$] (**1**) (see Figure 2) at relatively higher concentrations. The emission quantum yield (ϕ_{em}) of the free ligand L at ambient temperature, using 1,6-diphenyl 1,3,5-hexatriene (dpht) in MeCN as the standard, was found to be 0.0053, and that of the complex [ZnLCl$_2$] (**1**) was determined as 0.051 (see Supporting Information).

The blue shift of the emission band (504 nm) by complex **1** as compared to the emission band at 580 nm of free ligand L is quite unexpected (Figure 4), as one would expect the emission maximum of the free ligand L to be at higher energy relative to that of the complex because of its relatively high energy excitation band. This anomaly can be explained by the fact that excited states resulting from complexes of Zn(II) are typically ligand-centered (LC) in nature, owing to the inability of the d^{10} metal center to participate in low-energy charge-transfer or metal-centered transitions.[13] Therefore, the emission from [ZnLCl$_2$] (**1**) is believed to arise from an excited state, centered on L, which contains a phenolic proton (for the formula of L, see Scheme 1). It is well-established that the emissive organic phenol 2,6-diformyl-4-methylphenol undergoes a blue shift of its emission band (from 530 to 445 nm) upon treatment with a base B (e.g., piperidine or triethylamine), and this observation is interpreted to support the existence of an equilibrium between undissociated phenol and a proton-transferred species of phenol with the formation of phenoxide anion and BH$^+$ cation.[14] The same analogy can be extended to the present system, because the phenolic proton of the ligand L (Scheme 1) is deprotonated upon complexation with Zn^{2+} and this proton is transferred to the adjacent imine nitrogen (of the same ligand L) with the formation of NH$^+$. This proton transfer is also evidenced by IR spectral studies and crystal structure determination of complex [ZnLCl$_2$] (**1**; see Figure 1). Indeed, this proton is nicely located on uncoordinated imine nitrogen in the crystal structure of **1**. An emission experiment on the free ligand L in the presence of an added base, namely, triethylamine, in MeCN solution indicates the existence of an equilibrium between an undissociated L and a proton-transferred species of L (see Supporting Information).

We were interested to know whether the Zn(II) coordination center can be replaced by other metals, and we carried out similar syntheses[5] using other metal chlorides in place of ZnCl$_2$. However, we were not successful in obtaining crystalline compounds of [MLCl$_2$] for M = Mn^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+}.

In summary, we have designed and synthesized a chiral zinc complex, [ZnLCl$_2$] (**1**), that self-assembles via hydrogen bonding into supramolecular helices. It seems that the uncoordinated arm of the ligand plays an important role in forming these helices. Complex **1** not only shows chirality (circular dichroism at the molecular level and chiral helices at the supramolecular level), but also exhibits emission properties at room temperature.

Acknowledgment. We thank the Department of Science and Technology, Government of India, for financial support. The National X-ray Diffractometer facility at University of Hyderabad administered by the Department of Science and Technology, Government of India, is gratefully acknowledged. We are grateful to UGC, New Delhi, India, for providing the infrastructure facility at the University of Hyderabad and a fellowship to M.P. under a UPE grant. We thank Professor M. V. Rajashekaran for helpful discussions.

Supporting Information Available: X-ray crystallographic data for **1** (CIF). Text describing the synthesis and spectral data for ligand L and figures depicting concentration-dependent emission studies of ligand L and complex [ZnLCl$_2$] (**1**), quantum yield determinations of ligand L and complex [ZnLCl$_2$] (**1**), a figure of preliminary emission studies of ligand L with different metal ions (Mn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}). This material is available free of charge via the Internet at http://pubs.acs.org.

IC048236H

---

(13) (a) Dollberg, C. L.; Turro, C. *Inorg. Chem.* **2001**, *40*, 2484. (b) Roundhill, D. M. *Photochemistry and Photophysics of Metal Complexes*; Fackler, J. P., Ed.; Modern Inorganic Chemistry Series; Plenum Press: New York, 1994; pp 56−57.

(14) (a) Mukherjee, S. *Indian J. Chem.* **1987**, *26A*, 1002. (b) Das, R.; Mitra, S.; Mukherjee, S. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2492.