A Chiral Copper Complex Forms Supramolecular Homochiral Helices via O–H···Cl–Cu Interactions

Chullikkattil P. Pradeep,[a] Panthapally S. Zacharias,*[a] and Samar K. Das*[a]

Keywords: Copper / Helical structures / Hydrogen bonds / Schiff bases / Self-assembly / Supramolecular chemistry

An enantiopure ligand H_2L [Schiff base prepared from (*S*)-(+)-2-phenylglycinol and 2-hydroxy-5-nitrobenzaldehyde] reacts with $CuCl_2·2H_2O$ to yield a chiral copper complex [Cu(HL)Cl] (**1**) that forms right-handed supramolecular helices via O–H···Cl–Cu hydrogen bonds.

The influence of metal centers on hydrogen bonding has become a topic of intense research recently since metal-directed hydrogen bonding has far-reaching importance in inorganic supramolecular chemistry, materials chemistry, and bioinorganic chemistry. Metal-directed hydrogen bonding can show considerable strength and directionality and thereby is able to control the self-assembly of the building blocks, thus resulting in a variety of interesting supramolecular architectures.[1] Among these, hydrogen-bonded systems involving metal halides (M–X) have been well studied in materials chemistry and organometallic chemistry.[2] Halogens act as strong hydrogen-bond acceptors when bound to transition metals, in contrast to their limited ability to serve as weak hydrogen-bond acceptors when bound to carbon. The directional properties of metal halides in the formation of hydrogen bonds have been shown independently by the groups of Brammer and Orpen.[3]

Among the various metallo-supramolecular architectures, helical structures are of considerable interest because of their intrinsic chirality and their potential for yielding materials with novel chemical, electronic, biological, and optical properties.[4] Of particular interest are chiral helices prepared by the self-assembly of chiral building blocks.[5] We have recently reported a supramolecular homochiral helical architecture assembled by C–H···Cl–M hydrogen-bonding interactions.[6] However, to the best of our knowledge, there is no report on homochiral helices based on O–H···Cl–M interactions. In the present communication we wish to report a chiral, mononuclear, square-planar copper complex that self-assembles through O–H···Cl–Cu interactions to form homochiral helices in the crystal packing.

The reaction of a 1:1 mixture of (*S*)-(+)-2-phenylglycinol and 2-hydroxy-5-nitrobenzaldehyde in methanol yielded the tridentate chiral ligand H_2L in moderate yield. Reaction of H_2L with $CuCl_2·2H_2O$ in methanol at room temperature gave a green solid of [Cu(HL)Cl] (**1**), which on recrystallization from methanol gave X-ray quality crystals. The molecular structure of the complex is shown in Figure 1. The structure consists of a neutral, mononuclear, four-coordinate copper(II) complex with the chiral tridentate Schiff-base ligand providing the ONO donor atom set. The fourth position is occupied by a chloride ion. The overall coordination geometry of the compound is distorted square-planar, with the copper ion lying approximately at the center of the plane consisting of the ligand donor atoms Cl(1), O(1), N(1), and O(2).

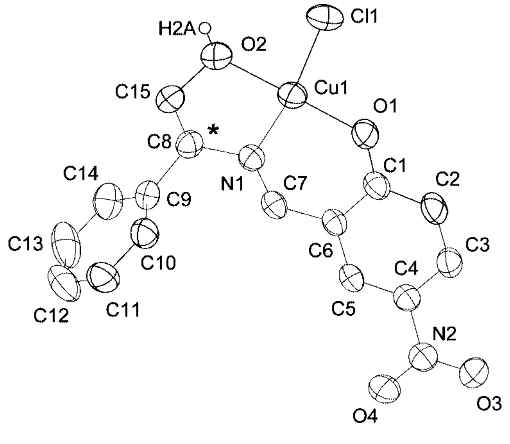


Figure 1. Thermal ellipsoidal plot (50%) of **1**. Hydrogen atoms are omitted for clarity. The asterisk mark indicates the chiral center. Selected bond lengths [Å] and angles [°]: Cu(1)–O(1) 1.880(2), Cu(1)–O(2) 1.968(2), Cu(1)–N(1) 1.954(2), Cu(1)–Cl(1) 2.2482(8), O(1)–C(1) 1.289(3), N(1)–C(7) 1.265(4); O(1)–Cu(1)–N(1) 94.04(9), O(1)–Cu(1)–O(2) 172.12(11), N(1)–Cu(1)–O(2) 81.37(10), O(1)–Cu(1)–Cl(1) 94.99(6), N(1)–Cu(1)–Cl(1) 170.74(7), O(2)–Cu(1)–Cl(1) 89.88(8).

---

[a] School of Chemistry, University of Hyderabad,
Hyderabad, 500046, India
Fax: +91-40-2301-2460
E-mail: skdsc@uohyd.ernet.in

Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

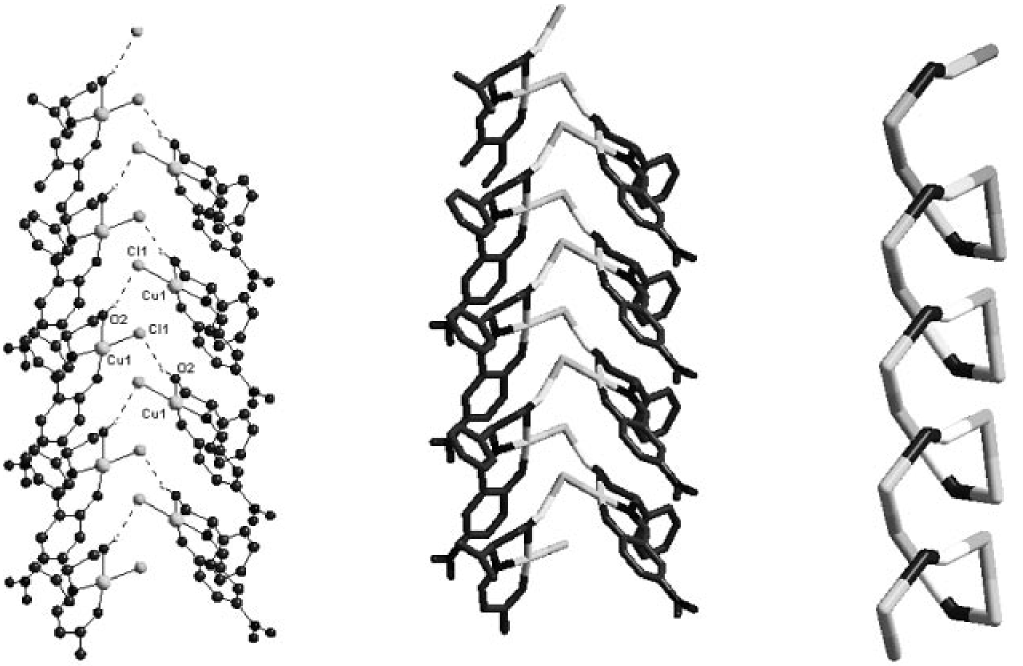


Figure 2. Intermolecular O–H···Cl–Cu hydrogen-bonding interactions between adjacent molecules that lead to the formation of homochiral helices. Ball-and-stick (left) and wire-frame (center) representations; helical backbone (right) (wire-frame representation).

The molecular packing in the crystal structure of **1** reveals strong O–H···Cl–Cu intermolecular hydrogen-bonding interactions involving the hydrogen atom on O(2) and the Cl(1) anion coordinated to the copper center (Figures 1 and 2). This results in the formation of supramolecular hydrogen-bonded helices that extend indefinitely throughout the crystal lattice (Figure 2) [selected hydrogen bonding parameters: H–O = 0.80(4) Å, H···Cl = 2.26(4) Å, O···Cl = 3.024(3) Å, and O–H···Cl = 159(4)°].

The O–H···Cl distance observed in this study [2.26(4) Å] is appreciably shorter than the sum of the van der Waals radii for the H and the neutral Cl atoms (2.95 Å). This can be classified as a strong interaction (those less than 2.52 Å are termed strong).[7a] Similar strong M–X···H–O bonds are known in the literature but they do not result in helical structures. Representative examples include a Cu–Cl···H–O hydrogen bond (H–O = 0.84 Å, H···Cl = 2.25 Å, O···Cl = 3.08 Å, and O–H···Cl = 173.3°) in the crystal structure of [CuCl($C_{19}H_{19}N_3O$)][7b] and a Cu–Cl···H–O hydrogen bond (H–O = 0.98 Å, H···Cl = 2.26 Å, O···Cl = 3.228 Å, and O–H···Cl = 171°) in the compound [CuCl($C_5H_9N_3$)($C_{12}H_8N_2$)]Cl·H_2O.[7c] The strength of the interaction can be attributed to the strong hydrogen-bond donor ability of the O–H group due to its greater acidity and to the strong H-bonding acceptor property of the metal-bound chloride.

The path of the helix can easily be traced by following the hydrogen bonds clockwise around the twofold screw axis of the helix. Three copper complex fragments form one helix turn in **1** with a pitch of 5.831 Å (Figure 2). We believe that the turn required to generate a perfect periodic self-assembly of [Cu(HL)Cl] (**1**) in a helical fashion is induced by the chirality of the building block coupled with the strong O–H···Cl–Cu hydrogen-bonding interactions. The rigidity of the Schiff-base ligand, which occupies three binding sites of the Cu atom, may also have some role in dictating such a helical arrangement in this self-assembly process. The absolute configuration of complex **1** was successfully determined by refining the Flack parameter [0.029(13)].[8]

Since we have described (above) a supramolecular helical feature of the copper complex [Cu(HL)Cl] (**1**) in the solid state, we decided to perform spectral studies in the solid state. The solid-state circular dichroism (CD) and electronic reflectance spectra of [Cu(HL)Cl] (**1**) are presented in Figure 3. The CD spectrum shows both positive and negative bands. The overall feature of the solid-state reflectance electronic spectrum is not identical to its solution spectrum (see Supporting Information). This can be correlated to the intermolecular interactions in the solid state of complex **1**, as shown in Figure 2. The bands observed in the electronic and CD spectra of complex **1** at around 700 nm are assigned to d–d transitions. The EPR spectrum (Figure 4) of a powdered sample of complex **1** at liquid nitrogen temperature exhibits a typical axial feature with $g_{\|} = 2.22$ and $g_{\perp} = 2.08$ for a Cu^{II} (d^9) system. The feature remains the same even at room temperature. The solution EPR spectrum (see Supporting Information) of complex **1** in frozen methanol shows an axial feature too, but with copper hyperfine coupling for a typical monomeric tetragonal Cu^{II} complex with a $d_{x^2-y^2}$ ground-state doublet.

To summarize, we have synthesized and characterized a chiral, mononuclear, square-planar Cu^{II} complex [Cu(HL)Cl] (**1**), which self-assembles through strong O–H···Cl–Cu intermolecular hydrogen-bonding interactions to form a homochiral helical arrangement. The advantages of this

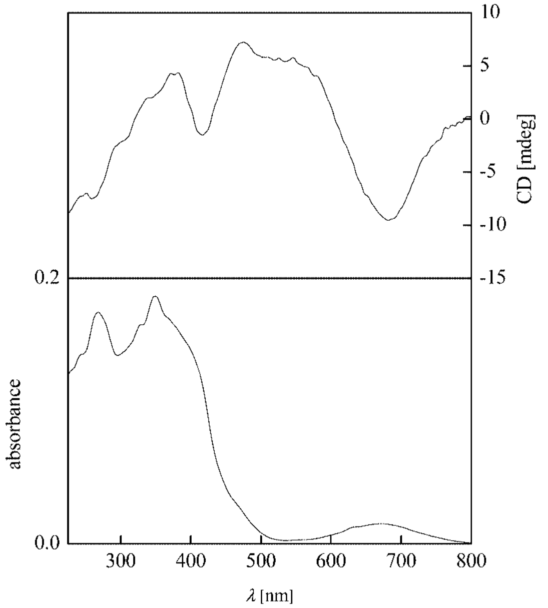


Figure 3. Circular dichroism and diffuse electronic reflectance spectra of **1** in the solid state (compound **1** was mixed with KBr to prepare a pellet).

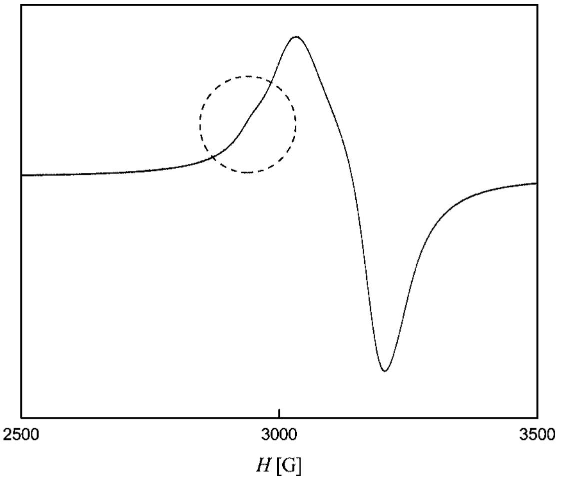


Figure 4. EPR spectrum of a powdered sample of **1** at liquid nitrogen temperature (the circle highlights the $g_{\|}$ feature).

system are that it is simple, easy to prepare, and provides potential for further explorations. The CD and electronic reflectance spectral studies (solid state vs. solution) of **1** support the intermolecular interactions in the solid state, which is consistent with the formation of supramolecular homochiral helices in the crystal. These intermolecular interactions may be lost in solution phase, as evidenced by EPR spectral studies.

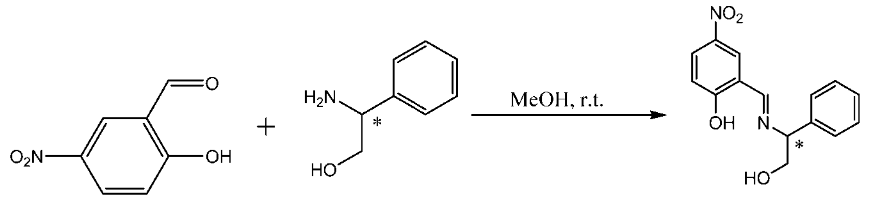
Experimental Section

General: Microanalytical (C, H, N) data were obtained with a Flash EA 1112 Series CHNS Analyzer. A Shimadzu 3101 PC UV/Vis/NIR spectrophotometer was used to record the electronic spectra. Infrared spectra were recorded on KBr pellets with a JASCO-5300 FT-IR spectrophotometer. ^{1}H NMR spectra of the ligand in $CDCl_3$ solution were recorded with a Bruker 400 MHz spectrometer using $Si(CH_3)_4$ as an internal standard. The CD spectra were measured with a JASCO J-810 spectropolarimeter. The EPR spectrum was recorded with a JEOL JES-FA200 spectrometer.

Synthesis of Enantiopure Ligand H_2L: (*S*)-(+)-2-Phenylglycinol (0.137 g, 1 mmol) and 2-hydroxy-5-nitrobenzaldehyde (0.167 g, 1 mmol) were stirred together in methanol (15 mL) at room temperature for 3 h. The resulting yellow solution was filtered and the filtrate was allowed to slowly concentrate. The resulting yellow solid was collected by filtration, washed with hexane, and dried at room temperature (0.25 g, 87%). $C_{15}H_{14}N_2O_4$ (286.28): calcd. C 62.93, H 4.93, N 9.79; found C 63.11, H 4.76, N 9.87. ^{1}H NMR ($CDCl_3$): δ = 4.00 (d, J = 7.2 Hz, 2 H, CH_2), 4.61 (t, J = 6.4 Hz, 1 H, CH), 7.00–7.45 (m, 6 H, Ar), 8.20–8.27 (m, 2 H, Ar), 8.52 (s, 1 H, H–C=N). IR (KBr): $\tilde{\nu}$ = 3272, 1649, 1615, 1545, 1350, 1225, 1070, 901, 835, 696 cm^{-1}. UV/Vis (CH_3OH): λ_{max} (ε) = 390 nm (6141 $M^{-1}cm^{-1}$), 324 (9655), 259 (18238), 240 (16123).

Synthesis of the Chiral Copper Complex [Cu(HL)Cl] (1): $CuCl_2 \cdot 2H_2O$ (0.17 g, 1 mmol) was added to a methanolic solution of the ligand H_2L (0.286 g, 1 mmol). The mixture was stirred at room temperature in air overnight. The resultant green solution gave a green, needle-shaped crystalline product on slow concentration, which was collected by filtration and recrystallized from methanol (0.265 g, 69%). $C_{15}H_{13}ClCuN_2O_4$ (384.27): calcd. C 46.88, H 3.41, N, 7.29; found C 47.02, H 3.49, N 7.18. IR (KBr): $\tilde{\nu}$ = 1634, 1600, 1549, 1468, 1387, 1308, 1094 cm^{-1}. Diffuse electronic reflectance (KBr pellet): λ_{max} = 270, 375, 700 nm. UV/Vis (CH_3CN): λ_{max} (ε) = 252 nm (20271 $M^{-1}cm^{-1}$), 235 (20105), 355 (18137), 690 (104).

X-ray Crystallographic Study: $C_{15}H_{13}ClCuN_2O_4$, M = 384.26 g mol^{-1}, monoclinic, space group $P2_1$, a = 11.3232(8), b = 5.8314(4), c = 12.3108(9) Å, β = 112.3110(10)°, V = 752.03(9) Å^3, Z = 2, $D_{calcd.}$ = 1.697 g cm^{-3}, μ = 1.651 mm^{-1}, $F(000)$ = 390, crystal size 0.31 × 0.08 × 0.08 mm. A total of 8757 reflections were collected of which 3368 unique reflections (R_{int} = 0.0262) were used. R = 0.0338 for 3056 reflections with $I > 2\sigma(I)$. Data were collected at 298(2) K with a Bruker SMART APEX CCD area detector system



H_2L

[λ(Mo-K_α) = 0.71073 Å] fitted with a graphite monochromator; 2400 frames were recorded with an ω-scan width of 0.3°, each for 15 s; crystal–detector distance: 60 mm; collimator: 0.5 mm. Data reduction with SAINTPLUS,[9] structure solution with SHELXS-97,[10] and refined with SHELXL-97.[11] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions and included in the refinement as riding on their respective parent atoms. The final Fourier difference synthesis showed minimum and maximum peaks of 0.566 and –0.223 e Å^{-3}. CCDC-265514 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

We thank the Department of Science and Technology, Government of India, for financial support. The National X-ray Diffractometer facility at the University of Hyderabad by the Department of Science and Technology, Government of India, is also gratefully acknowledged. We are grateful to UGC, New Delhi, for providing infrastructure facilities at the University of Hyderabad under UPE grant. C. P. P. thanks UGC, New Delhi, for a fellowship.

---

[1] a) L. Brammer, *Chem. Soc. Rev.* **2004**, *33*, 476–489; b) L. Brammer, *Dalton Trans.* **2003**, 3145–3157; c) L. M. Epstein, E. S. Shubina, *Coord. Chem. Rev.* **2002**, *231*, 165–181; d) D. Braga, F. Grepioni, *Acc. Chem. Res.* **2000**, *33*, 601–608; e) R. H. Crabtree, P. E. M. Siegbahn, O. Eisenstein, A. L. Rheingold, T. F. Koetzle, *Acc. Chem. Res.* **1996**, *29*, 348–354; f) A. D. Burrows, C.-W. Chan, M. M. Chowdhry, J. E. McGrady, D. M. P. Mingos, *Chem. Soc. Rev.* **1995**, *24*, 329–339.

[2] U. Bentrup, M. Feist, E. Kemnitz, *Prog. Solid State Chem.* **1999**, *27*, 75–129; L. Brammer, E. A. Bruton, P. Sherwood, *Cryst. Growth Des.* **2001**, *1*, 277–290; R. Kuhlman, *Coord. Chem. Rev.* **1997**, *167*, 205–232; M. J. Riley, D. Neill, P. V. Bernhardt, K. A. Byriel, C. H. L. Kennard, *Inorg. Chem.* **1998**, *37*, 3635–3639; D. V. Yandulov, K. G. Caulton, N. V. Belkova, E. S. Shubina, L. M. Epstein, D. V. Khoroshum, D. G. Musaev, K. Morokuma, *J. Am. Chem. Soc.* **1998**, *120*, 12553–12563; D.-H. Lee, H. J. Kwon, B. P. Patel, L. M. Liable-Sands, A. L. Rheingold, R. H. Crabtree, *Organometallics* **1999**, *18*, 1615–1621; Z. Mazej, K. L. Borrmann, B. Zemva, *Inorg. Chem.* **1998**, *37*, 5912–5914.

[3] J. C. Mareque Rivas, L. Brammer, *Inorg. Chem.* **1998**, *37*, 4756–4757; G. R. Lewis, A. G. Orpen, *Chem. Commun.* **1998**, 1873–1874; A. L. Gillon, A. G. Orpen, J. Starbuck, X.-M. Wang, Y. Rodríguez-Martín, C. Ruiz-Pérez, *Chem. Commun.* **1999**, 2287–2288; A. L. Gillon, G. R. Lewis, A. G. Orpen, S. Rotter, J. Starbuck, X.-M. Wang, Y. Rodríguez-Martín, C. Ruiz-Pérez, *J. Chem. Soc., Dalton Trans.* **2000**, 3897–3905; A. Angeloni, A. G. Orpen, *Chem. Commun.* **2001**, 343–344.

[4] J.-M. Lehn, *Supramolecular Chemistry − Concepts and Perspectives*, VCH, Weinheim, **1995**; E. C. Constable, in *Comprehensive Supramolecular Chemistry* (Eds.: J. P. Sauvage, M. W. Hosseini), Pergamon Press, Oxford, **1996**, vol. 9, p. 213–252; E. C. Constable, C. E. Housecroft, M. Neuburger, D. Phillips, P. R. Raithby, E. Schofield, E. Sparr, D. A. Tocher, M. Zehnder, Y. Zimmermann, *J. Chem. Soc., Dalton Trans.* **2000**, 2219–2228; C. Piguet, J.-C. G. Bünzli, *Chem. Soc. Rev.* **1999**, *28*, 347–358; M. Albrecht, *Chem. Rev.* **2001**, *101*, 3457–3497; M. J. Hannon, V. Moreno, M. J. Prieto, E. Moldrheim, E. Sletten, I. Meistermann, C. J. Isaac, K. J. Sanders, A. Rodger, *Angew. Chem. Int. Ed.* **2001**, *40*, 879–884.

[5] U. Knof, A. von Zelewsky, *Angew. Chem. Int. Ed.* **1999**, *38*, 302–322; C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* **1997**, *97*, 2005–2062; G. Baum, E. C. Constable, D. Fenske, C. E. Housecroft, T. Kulke, *Chem. Eur. J.* **1999**, *5*, 1862–1873 and references cited therein.

[6] M. Prabhakar, P. S. Zacharias, S. K. Das, *Inorg. Chem.* **2005**, *44*, 2585–2587.

[7] a) G. Aullón, D. Bellamy, L. Brammer, E. A. Bruton, A. G. Orpen, *Chem. Commun.* **1998**, 653–654; b) M. M. Olmstead, T. E. Patten, C. Troeltzsch, *Inorg. Chim. Acta* **2004**, *357*, 619–624; c) E. Y. Bivián-Castro, S. Bernès, J. Escalante, G. Mendoza-Díaz, *Acta Crystallogr., Sect. C* **2004**, *60*, m205–m207.

[8] H. D. Flack, *Acta Crystallogr., Sect. A* **1983**, *39*, 876–881.

[9] Software for the CCD Detector System, Bruker Analytical X-ray Systems Inc., Madison, WI, **1998**.

[10] G. M. Sheldrick, *Program for structure solution*, University of Göttingen, Germany, **1997**.

[11] G. M. Sheldrick, *Program for crystal structure analysis*, University of Göttingen, Germany, **1997**.

Received: March 25, 2005