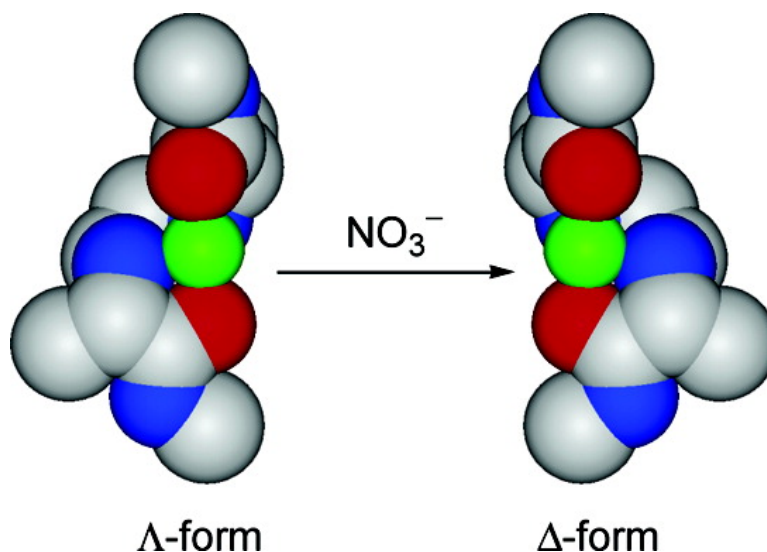


Dynamic Helicity Inversion by Achiral Anion Stimulus in Synthetic Labile Cobalt(II) Complex

Hiroyuki Miyake, Kana Yoshida, Hideki Sugimoto, and Hiroshi Tsukube

J. Am. Chem. Soc., **2004**, 126 (21), 6524-6525 • DOI: 10.1021/ja049130o • Publication Date (Web): 11 May 2004

Downloaded from <http://pubs.acs.org> on March 31, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 5 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



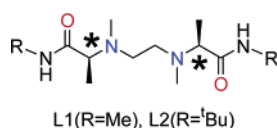
Dynamic Helicity Inversion by Achiral Anion Stimulus in Synthetic Labile Cobalt(II) Complex

Hiroyuki Miyake,* Kana Yoshida, Hideki Sugimoto, and Hiroshi Tsukube

Department of Chemistry, Graduate School of Science, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

Received February 17, 2004; E-mail: miyake@sci.osaka-cu.ac.jp

Natural supramolecules such as DNAs and proteins often have ordered helical structures, and inversion of the helical direction is thought to play key roles in gene expression and cellular processes.¹ Although the helicities of these molecules, whether right- or left-handed, are generally determined by the stereochemistry of the components, external stimuli also alter the helix sense. For example, the left-handed DNA, Z-DNA, is derived from a right-handed helix by salt enrichment, cytosine methylation, and complexation with spermine, spermidine, and metal cations.² Similarly, the helical direction of the left-handed polyproline II structure changes, depending on the polarity of the medium.³ Several artificial systems offering helicity inversion by external stimuli have been reported recently.⁴ Yashima et al.^{4c,d} and Fujiki et al.^{4e} demonstrated that the helicities of polyacetylenes and polysilylenes can be inverted by the addition of chiral amines and by temperature changes. Such helicity inversion systems provide further insights into the chemical understanding of biologically sophisticated processes and represent the basis for the development of supramolecular sensors, catalysts, switches, and memory devices. This communication reports that the helicity of a synthetic Co(II) complex with chiral tetradentate ligand L1 is dynamically and efficiently inverted by simply adding achiral NO₃⁻ anion. Several types of metal complexes have been shown to offer helicity inversion induced by external stimuli.⁵ However, these previous examples included the kinetically inert Co(III) and Cr(III) centers, and rendered the inversion processes slow and incomplete. In contrast, the kinetically labile Co(II) complex allows dynamic and efficient helicity inversion (as demonstrated in this report), which is required for application to supramolecular switching devices.



The chiral tetradentate N₂O₂ ligand L1⁶ including secondary amide groups external to the ethylenediamine part formed a pseudo-octahedral complex with the Co(II) cation. This complex was crystallized from a CH₃OH solution of L1 and Co(ClO₄)₂·6H₂O. Its X-ray crystal structure analysis revealed that the Co(II) center is coordinated by two amine nitrogens and two amide oxygens from the ligand, adopting a Λ *cis*- α configuration around the Co(II) center (Figure 1). The other two coordination sites are occupied by two oxygen atoms of the two CH₃OH molecules present as the solvent, with two counter perchlorate anions outside of the coordination sphere. In the ¹H NMR spectrum of the L1–Co(ClO₄)₂ complex recorded in CD₃CN/CD₂Cl₂ = 1/9, all signals appeared in the region –50 to 160 ppm with C₂ symmetric patterns, except for a signal of the released CH₃OH.⁷ Since only weak signals with C₂ symmetry due to the minor diastereomeric isomer were observed (<2.5%), this complex retained an asymmetric helical structure in solution.

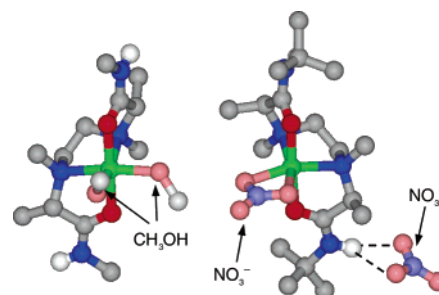


Figure 1. Crystal structures of [Co(L1)(CH₃OH)₂](ClO₄)₂·(CH₃OH)₂ (left) and [Co(L2)(NO₃)](NO₃)·(CH₃CN) (right). Most hydrogen atoms and solvent molecules are omitted for simplification.

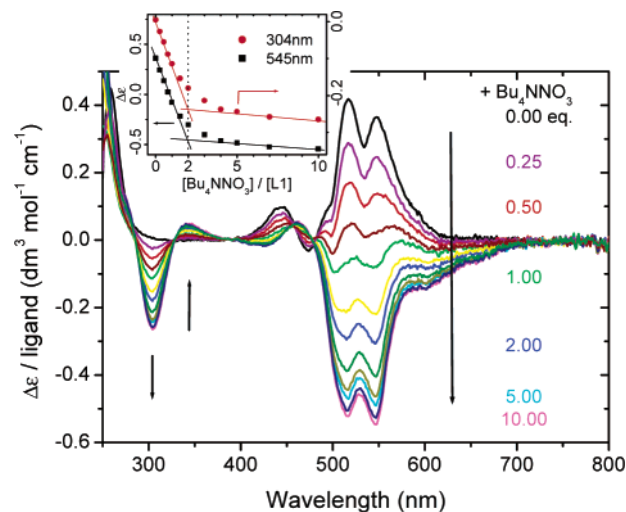
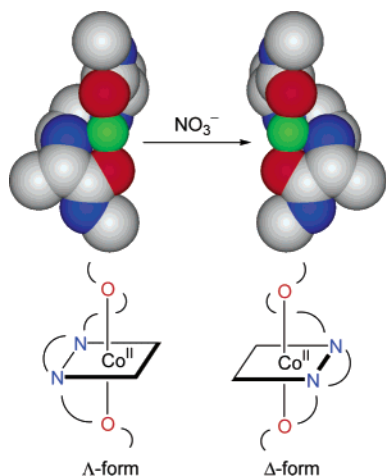


Figure 2. CD spectral changes of 1:1 mixture of L1 and Co(ClO₄)₂·6H₂O (black) upon the addition of Bu₄NNO₃ in CH₃CN/CH₂Cl₂ = 1/9 at room temperature. (Inset) Titration profiles of the CD amplitudes at 304 and 545 nm. [L1] = [Co(ClO₄)₂·6H₂O] = 1.5 × 10⁻³ mol dm⁻³.

This L1–Co(ClO₄)₂ complex exhibited a positive CD signal in the range of the d–d transition (around 530 nm) in CH₃CN/CH₂Cl₂ = 1/9 (Figure 2). The sense of the observed CD spectra changed dramatically from positive to negative upon the addition of NO₃⁻ anion as an external stimulus, suggesting that the addition of achiral NO₃⁻ anion induced the helicity inversion of the labile Co(II) complex from Λ to Δ form (Scheme 1).⁸ The ¹H NMR spectrum of this complex in the presence of 10 equiv of Bu₄NNO₃ clearly showed that almost complete inversion of helicity (Δ/Λ form = 85/15) was achieved within one minute at room temperature. When Cl⁻ and Br⁻ anions were added to the L1–Co(ClO₄)₂ solution, UV–vis spectra showed the formation of tetrahedral species in addition to octahedral ones, while AcO⁻ anion accelerated the oxidation of Co(II) to Co(III). The addition of excess ClO₄⁻ and BF₄⁻ anions had little effect on the CD spectral shape or intensity

Scheme 1. Helicity Inversion Achieved by Achiral NO_3^- Anion

of the $\text{L1-Co}(\text{ClO}_4)_2$ complex, indicating that the NO_3^- anion acted as a specific external stimulus to invert the chirality at the metal center. Similar helicity inversion was observed with $\text{Ni}(\text{II})$ and $\text{Cu}(\text{II})$ complexes. The sense of CD spectra on $\text{L1-Ni}(\text{ClO}_4)_2$ and $\text{L1-Cu}(\text{ClO}_4)_2$ complexes was reversed upon the addition of NO_3^- anion. Figure 2 also indicates that the induced CD signal was also observed at 280–360 nm due to an absorption of the NO_3^- anion, possibly reflecting the fixation of the NO_3^- anion around the chiral centers of the $\text{Co}(\text{II})$ complex. Titration experiments showed that 2 equiv of NO_3^- anion is required to induce complete chirality inversion of this metal complex (inset of Figure 2). The cooperative actions of two NO_3^- anions for coordination to the $\text{Co}(\text{II})$ center and hydrogen bondings with amide hydrogen were demonstrated to stabilize the Δ form more effectively than the corresponding Λ form in $\text{L2-Co}(\text{NO}_3)_2$ complex (Figure 1).⁹ The binding of the NO_3^- anion with the amide hydrogen causes steric repulsion with a substituent to destabilize the Λ form, while the bidentate chelation of the NO_3^- anion to the $\text{Co}(\text{II})$ center with a small bite angle moderates steric hindrance around the $\text{Co}(\text{II})$ center in the Δ form.

When optically active ligands form chiral metal complexes with defined stereochemistry, the resulting complexes are usually static and generally require high temperature, highly polar media, long periods, and severe conditions to induce helicity inversion.^{5a,10} The present results demonstrated that the helical chirality of the kinetically labile $\text{Co}(\text{II})$ complex is dynamically invertible by an external stimulus within one minute. $\text{Co}(\text{II})$ complexes have been applied as highly stereoselective catalysts,^{11a} effective building-block cores for molecular architecture,^{11b} specific redox devices, electron-transfer mediators, and ion sensors.^{11c,d} A dynamic and efficient helicity inversion system as presented in this report is therefore a promising step toward the design of supramolecular devices.

Acknowledgment. We are grateful to Professor Isamu Kinoshita of Osaka City University and Professor Hitoshi Tamiaki of Ritsumeikan University for comments on CD measurements. This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information Available: Synthetic procedures, X-ray analysis data of $[\text{Co}(\text{L1})(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2 \cdot (\text{CH}_3\text{OH})_2$ and $[\text{Co}(\text{L2})(\text{NO}_3)](\text{NO}_3) \cdot (\text{CH}_3\text{CN})$ complexes (CIF and PDF) and CD spectra of $\text{L2-Co}(\text{ClO}_4)_2$ and $\text{L2-Co}(\text{NO}_3)_2$ complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Rich, A.; Zhang, S. *Nat. Rev. Genet.* **2003**, *4*, 566. (b) Pawson, T.; Nash, P. *Science* **2003**, *300*, 445.
- (2) Mahadevan, S.; Palaniandavar, M. *Inorg. Chem.* **1998**, *37*, 3927.
- (3) (a) Traub, W.; Shmueli, U. *Nature* **1963**, *198*, 1165. (b) Cowan, P. M.; McGavin, S. *Nature* **1955**, *176*, 501.
- (4) (a) Feringa, B. L.; van Delden, R. A.; Koumura, N.; Geertsema, E. M. *Chem. Rev.* **2000**, *100*, 1789. (b) Zahn, S.; Canary, J. W. *Science* **2000**, *288*, 1404. (c) Yashima, E.; Maeda, K.; Okamoto, Y. *Nature* **1999**, *399*, 449. (d) Ishikawa, M.; Maeda, K.; Mitsutsuji, Y.; Yashima, E. *J. Am. Chem. Soc.* **2004**, *126*, 732. (e) Fujiki, M.; Koe, J. R.; Motonaga, M.; Nakashima, H.; Terao, K.; Teramoto, A. *J. Am. Chem. Soc.* **2001**, *123*, 6253. (f) Borovkov, V. V.; Hembury, G. A.; Inoue, Y. *Angew. Chem., Int. Ed.* **2003**, *42*, 5310. (g) Preston, A. J.; Fraenkel, G.; Chow, A.; Gallucci, J. C.; Parquette, J. R. *J. Org. Chem.* **2003**, *68*, 22. (h) Tang, K.; Green, M. M.; Cheon, K. S.; Selinger, J. V.; Garetz, B. A. *J. Am. Chem. Soc.* **2003**, *125*, 7313. (i) Crespo, L.; Sanclimens, G.; Montaner, B.; Pérez-Tomás, R.; Royo, M.; Pons, M.; Albericio, F.; Giralt, E. *J. Am. Chem. Soc.* **2002**, *124*, 8876. (j) Seeman, N. C. *Nature* **2003**, *421*, 427. (k) Inai, Y.; Ousaka, N.; Okabe, T. *J. Am. Chem. Soc.* **2003**, *125*, 8151. (l) Li, J.; Schuster, G. B.; Cheon, K. S.; Green, M. M. *Selinger, J. V. J. Am. Chem. Soc.* **2000**, *122*, 2603.
- (5) (a) Aldrich-Wright, J. R.; Vagg, R. S.; Williams, P. A. *Coord. Chem. Rev.* **1997**, *166*, 361. (b) Benedetti, M.; Biscarini, P.; Brillante, A.; Castiglioni, E. *Enantiomer* **1999**, *4*, 63. (c) Biscarini, P.; Kuroda, R. *Inorg. Chim. Acta* **1988**, *154*, 209. (d) Kita, M.; Yamamori, K. *J. Chem. Soc., Dalton Trans.* **1999**, 1221. (e) Anzai, N.; Machida, S.; Horie, K. *Chem. Lett.* **2001**, 888.
- (6) Its ^1H and ^{13}C NMR spectra indicated its stereochemical purity to be >98% de.
- (7) ^1H NMR signal corresponding to free CH_3OH molecules was observed at 3.5 ppm, indicating the rapid replacement of two CH_3OH molecules by two CH_3CN molecules.
- (8) $\text{L1-Co}(\text{ClO}_4)_2$ complex showed the same CD sign in CH_3OH and water, although it is not soluble in nonpolar solvents. Changing the complex concentration rarely altered the helicity of the complex.
- (9) $\text{L2-Co}(\text{ClO}_4)_2$ complex exhibited a CD signal with the sign opposite to that of $\text{L2-Co}(\text{NO}_3)_2$ complex in CH_3CN (Figure S3).
- (10) (a) Knof, U.; von Zelewsky, A. *Angew. Chem., Int. Ed.* **1999**, *38*, 302. (b) Telfer, S. G.; Sato, T.; Kuroda, R.; Lefebvre, J.; Leznoff, D. B. *Inorg. Chem.* **2004**, *43*, 421. (c) Chin, J.; Lee, S. S.; Lee, K. J.; Park, S.; Kim, D. H. *Nature* **1999**, *401*, 254. (d) Cornelissen, J. J. L. M.; Rowan, A. E.; Nolte, R. J. M.; Sommerdijk, N. A. J. M. *Chem. Rev.* **2001**, *101*, 4039. (e) Tanaka, K.; Tengeiji, A.; Kato, T.; Toyama, N.; Shionoya, M. *Science* **2003**, *299*, 1212. (f) Knight, P. D.; Scott, P. *Coord. Chem. Rev.* **2003**, *242*, 125.
- (11) (a) Yoon, T. P.; Jacobsen, E. N. *Science* **2003**, *299*, 1691. (b) Kitagawa, S.; Kawata, S. *Coord. Chem. Rev.* **2002**, *224*, 11. (c) Kume, S.; Kurihara, M.; Nishihara, H. *Chem. Commun.* **2001**, 1656. (d) Shioya, T.; Swager, T. M. *Chem. Commun.* **2002**, 1364. (e) Sapp, S. A.; Elliott, C. M.; Contado, C.; Caramori, S.; Bignozzi, C. A. *J. Am. Chem. Soc.* **2002**, *124*, 11215.

JA0491300