Drastic Structural Change in Silver(I) Complexes with Alteration of the Optical Activity of a Pyridine Derivative Ligand: Helical Arrays with Extended Structure and an Optically Inactive Dinuclear Complex

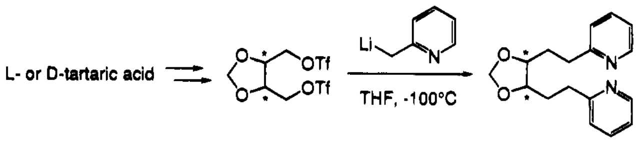
Takayoshi Suzuki,[1a] Hiyoshizo Kotsuki,*[,1b] Kiyoshi Isobe*[,1a] Narimasa Moriya,[1b] Yuichi Nakagawa,[1b] and Masamitsu Ochi[1b]

Institute for Molecular Science, Okazaki 444, Japan, and Department of Chemistry, Faculty of Science, Kochi University, Kochi 780, Japan

Received June 9, 1994

In recent years there has been a renewal of interest in helical chirality in inorganic and coordination chemistry.[2-4] Helicates,[4a] which are polynuclear metal complexes having helical topology of the ligands, not only are the objects of molecular architecture but also are utilized as asymmetric catalysts.[5,6] Although a variety of helicates have been reported,[4,5] most of the works have been limited to racemic mixtures of the left-handed and right-handed ones. Except for the spontaneous resolution of the helicates,[2,4d] only two precedents have been reported for the enantiospecific synthesis of helicates using diastereoisomerism with optical activity of a bridging ligand,[4c,5] and therefore, the relationship between helicity of helicates and chirality of ligands has not been well-known. Moreover, the role of optical activity (either an enantiomerically pure form or a racemic mixture) of the ligand in the structures of such complexes has not been understood. In order to elucidate the relationship and the role of optical activity of the ligand, we designed C_2 symmetric didentate ligands, *(4R,5R)*- and *(4S,5S)*-4,5-bis(2-(2-pyridyl)ethyl)-1,3-dioxolane (**R,R-L** and **S,S-L**), prepared silver(I) complexes with the ligands, and characterized the structures of these complexes by X-ray analysis. As a consequence, a remarkable structural change in the silver(I) complexes was observed: helical arrays with extended structure for the enantiomerically pure ligands and an optically inactive dinuclear complex for the racemic mixture of the ligand.

Scheme 1



R,R-L or S,S-L

The ligands were prepared from L- or D-tartaric acid *via* coupling reaction of chiral triflate intermediates[7] (Scheme 1). Treatment of the optically pure ligand (**R,R-L** or **S,S-L**) with silver(I) trifluoromethanesulfonate (AgOTf) in methanol gave colorless prismatic crystals in nearly quantitative yield.[8] The X-ray diffraction analyses[9] of these complexes revealed that they are crystallized in the orthorhombic space group $P2_12_12_1$ with the same lattice constants (within the standard deviations) and are completely enantiotopic with each other. Each complex cation has an extended structure[10] consisting of Ag^+ with a slightly distorted linear geometry and the bridging ligands as shown in Figure 1a for [{Ag(**R,R-L**)}$_\infty$](OTf)$_\infty$. The Ag^+ cation has a weak interaction with the O atom in OTf^- (the shortest distance between them is 2.893(8) Å). The array with extended structure runs toward a crystallographic 2-fold screw axis, but the Ag^+ ion is not sited on the axis and the extended array has a "helical" structure. Projection of the array along the screw axis for each isomer exhibits the left-handed helicity for [{Ag(**R,R-L**)}$_\infty$](OTf)$_\infty$ (Figure 1b) and the right-handed for [{Ag(**S,S-L**)}$_\infty$](OTf)$_\infty$. In addition, the bridging ligands at both sides of the main helix also have peripherally helical conformations: the **R,R-L** ligand has a right-handed helicity, and the **S,S-L**, a left-handed helicity. There is no doubt that the peripheral helicity in the bridges as well as the helicity in the extended arrays is induced stereospecifically by the asymmetric nature of the didentate pyridine ligand.

From a similar reaction with a racemic mixture of the ligands (**rac-L**), a 1:1 mixture of **R,R-L** and **S,S-L**, colorless prismatic crystals were obtained.[8] X-ray analysis[9] confirmed that the crystal has a monoclinic centrosymmetric space group, $P2_1/c$. The complex is not a mixture of [{Ag(**R,R-L**)}$_\infty$](OTf)$_\infty$ and [{Ag(**S,S-L**)}$_\infty$](OTf)$_\infty$ but has a completely different dinuclear

---

(1) (a) Institute for Molecular Science. (b) Kochi University.

(2) Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J.; O'Connor, C. J. *Science* **1993**, *259*, 1596.

(3) (a) Deuschel-Cornioley, C.; Stoeckli-Evans, H.; von Zelewsky, A. *J. Chem. Soc., Chem. Commun.* **1990**, 121. (b) Wester, D.; Palenik, G. J. *J. Chem. Soc., Chem. Commun.* **1975**, 74. (c) Judice, J. K.; Keipert, S. J.; Cram, D. J. *J. Chem. Soc., Chem. Commun.* **1993**, 1323.

(4) (a) Youinou, M.-T.; Ziessel, R.; Lehn, J.-M. *Inorg. Chem.* **1991**, *30*, 2144 and references cited therein. (b) Baxter, P.; Lehn, J.-M.; De Cian, A.; Fischer, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 69. (c) Zarges, W.; Hall, J.; Lehn, J.-M.; Bolm, C. *Helv. Chim. Acta* **1991**, *74*, 1843. (d) Krämer, R.; Lehn, J.-M.; De Cian, A.; Fischer, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 703. (e) Constable, E. C. *Tetrahedron* **1992**, *48*, 10013. (f) Constable, E. C.; Hannon, M. J.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1993**, 1883 and references cited therein. (g) Piguet, C.; Bünzli, J.-C. G.; Bernardinelli, G.; Hopfgartner, G.; Williams, A. F. *J. Am. Chem. Soc.* **1993**, *115*, 8179 and references cited therein. (h) Potts, K. T.; Keshavarz-K, M.; Tham, F. S.; Raiford, K. A. G.; Arana, C.; Abruña, H. D. *Inorg. Chem.* **1993**, *32*, 5477 and references cited therein. (i) Serr, B. R.; Andersen, K. A.; Elliott, C. M.; Anderson, O. P. *Inorg. Chem.* **1988**, *27*, 4499. (j) Crane, J. D.; Sauvage, J.-P. *New J. Chem.*, **1992**, *16*, 649. (k) Carrad, L. H.; Goodgame, D. M. L.; Hill, S. P. W.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1993**, 1003 and references cited therein.

(5) Corey, E. J.; Cymin, C. L.; Noe, M. C. *Tetrahedron Lett.* **1994**, *35*, 69.

(6) Maruoka, K.; Murase, N.; Yamamoto, H. *J. Org. Chem.* **1993**, *58*, 2938.

(7) Kotsuki, H.; Nishikawa, H.; Mori, Y.; Ochi, M. *J. Org. Chem.* **1992**, *57*, 5036 and references cited therein.

(8) See supplementary material.

(9) Crystallographic data for [{Ag(**R,R-L**)}$_\infty$](OTf)$_\infty$: fw = 541.3 × n, orthorhombic, space group $P2_12_12_1$, $a = 13.065(5)$ Å, $b = 18.684(7)$ Å, $c = 8.810(5)$ Å, $V = 2151(2)$ Å^3, $D_x = 1.67$ Mg m^{-3}, $Z = 4$ (for the [Ag(**R,R-L**)]OTf unit), μ(Mo Kα) = 1.09 mm^{-1}, and R (R_w) = 0.058 (0.065) for 2524 independent unique reflections ($|F_o| > 3\sigma(|F_o|)$). Crystallographic data for [{Ag(**S,S-L**)}$_\infty$](OTf)$_\infty$: fw = 541.3 × n, orthorhombic, space group $P2_12_12_1$, $a = 13.063(3)$ Å, $b = 18.689(5)$ Å, $c = 8.817(3)$ Å, $V = 2153(2)$ Å^3, $D_x = 1.67$ Mg m^{-3}, $Z = 4$ (for the [Ag(**S,S-L**)]OTf unit), μ(Mo Kα) = 1.09 mm^{-1}, and R (R_w) = 0.059 (0.065) for 2485 independent unique reflections ($|F_o|] > 3\sigma(|F_o|)$). Crystallographic data for [Ag$_2$(**rac-L**)$_2$](OTf)$_2$: fw = 1082.6, monoclinic, space group $P2_1/c$, $a = 9.281(5)$ Å, $b = 23.518(6)$ Å, $c = 9.802(6)$ Å, $\beta = 105.82(2)°$, $V = 2058(2)$ Å^3, $D_x = 1.75$ Mg m^{-3}, $Z = 2$ (for the dimer unit), μ(Mo Kα) = 1.14 mm^{-1}, and R (R_w) = 0.065 (0.062) for 2563 independent unique reflections ($|F_o| > 3\sigma(F_o|)$).

(10) The silver complex with an extended array has already been synthesized by using the achiral didentate ligand *trans*-1,2-bis-(2-pyridyl)ethylene: Kitagawa, S.; Matsuyama, S.; Munakata, M.; Emori, T. *J. Chem. Soc., Dalton Trans.* **1991**, 2869.

0020-1669/95/1334-0530$09.00/0

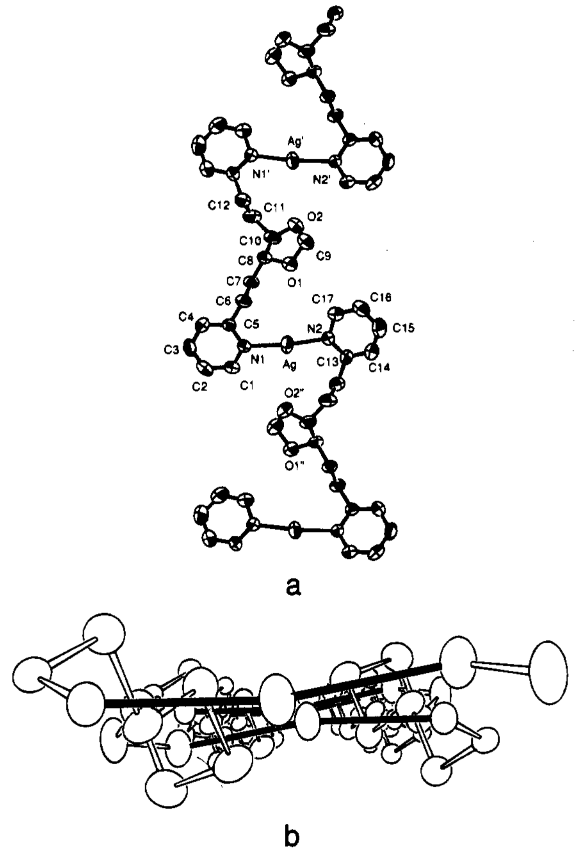


Figure 1. Perspective drawings of the helically extended array in [{Ag(**R,R-L**)}$_\infty$](OTf)$_\infty$: (a) from the side of the crystallographic *b* axis that is a 2-fold screw axis; (b) along the axis (for (b) only a part of the array is shown for clarity).

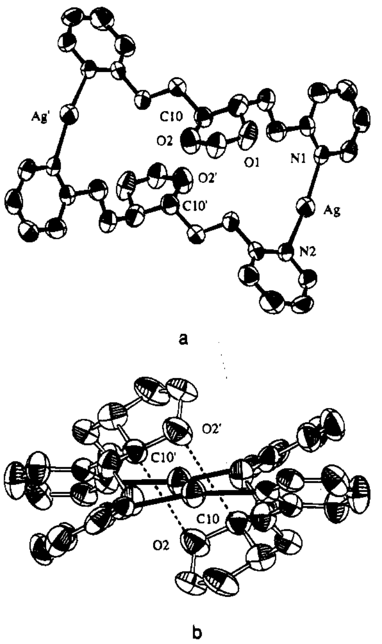


Figure 2. Perspective drawings of the complex cation in [Ag$_2$(**rac-L**)$_2$](OTf)$_2$: (a) top view; (b) side view.

structure with an inversion center, [Ag$_2$(**rac-L**)$_2$](OTf)$_2$ (Figure 2). Since the two bridging ligands consist of a pair of each enantiomer (**R,R-L** and **S,S-L**), the complex should have a meso-formed dinuclear framework. No methanolic solution of one single crystal is circular dichroism active, which indicates that the optically inactive dinuclear complex is specifically formed.

The drastic structural change of the complexes, that is, the helically extended arrays and the dinuclear complex, is just accompanied by an alteration of optical activity of the ligands used in complexation. Why does not the reaction with an enantiomerically pure ligand form a dinuclear complex ([Ag$_2$(**R,R-L**)$_2$](OTf)$_2$ or [Ag$_2$(**S,S-L**)$_2$](OTf)$_2$)? Why does not the reaction with **rac-L** yield a racemic mixture of each helical array, although the arrays have lower solubility? As shown in Figure 2 the two dioxolane rings in the bridging ligands (**R,R-L** and **S,S-L**) in the dinuclear complex are close to each other. Molecular recognition which stabilizes the dinuclear framework probably exists between **R,R-L** and **S,S-L** by the assistance of the two Ag$^+$ ions. The distance between H10 and O2' is 2.491(7) Å, shorter than the sum of a van der Waals radius of H and O (2.72 Å),[11] and the angle of C10–O2$\cdot\cdot$H10' is 103.7(5)°. This might suggest the presence of a hydrogen bond-like interaction between these atoms,[8,12] and the recognition between the two ligands might be ascribable to such an interaction stabilizing the meso-formed dinuclear framework. On the other hand, a presumed dinuclear structure of [Ag$_2$(**R,R-L**)$_2$](OTf)$_2$ or [Ag$_2$(**S,S-L**)$_2$](OTf)$_2$ may give rise to a serious repulsion between the dioxolane rings. Thus, the preferential formation of helically extended arrays in the reaction with **R,R-L** or **S,S-L** is reasonable.

Mixing of methanolic solutions of [{Ag(**R,R-L**)}$_\infty$](OTf)$_\infty$ and [{Ag(**S,S-L**)}$_\infty$](OTf)$_\infty$ (1:1) also provided the same meso-formed dinuclear complex, [Ag$_2$(**rac-L**)$_2$](OTf)$_2$, as that from the racemic ligand and AgOTf.[8] This indicates that the extended structure is not maintained in solution. Both ^{1}H NMR and CD spectroscopic titrations for the systems of AgOTf and any free **L** display the formation of 1:1 ([AgOTf]:[L]) species in methanol.[8] All complexes described above give the same ^{1}H NMR, NOESY NMR, or electronic spectra as one another in methanol because of the fluxionality based on a rapid cleavage and recombination of the Ag–N bond.[8] Further studies on the structures in solution of these complexes are in progress. The conditions required to form the specific structures in the solid state are met upon crystallization of the complex from the methanolic solution, where the interligand steric effect and the hydrogen bond-like interaction induced by the asymmetric centers of the ligands may play an important role.

Acknowledgment. The authors are grateful to Professor Akira Nagasawa (Saitama University) for helpful discussions about solution chemistry. They also thank Professor Masaaki Kojima (Okayama University) and Mr. Shin-ichi Masuzawa (JEOL) for CD and NOESY measurements, respectively. This work was partly supported by Grant-in-Aids for Scientific Research No. 06854037 from the Ministry of Education, Science, and Culture of Japan. One of the authors (H.K.) acknowledges the support of his work by the Tanabe Seiyaku Award in Organic Chemistry (Japan).

Supplementary Material Available: Descriptions of X-ray analyses, including tables of experimental and refinement conditions, atomic coordinates, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom locations and ORTEP drawings, ORTEP drawings of another helically extended array with a different anion, [{Ag(**S,S-L**)}$_\infty$](PF$_6$)$_\infty$, and text describing experimental procedures and figures showing spectra for the infrared, ^{1}H NMR, NOESY, and CD measurements (53 pages). Ordering information is given on any current masthead page.

IC940667K

---

(11) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(12) (a) Sutor, D. J. *Nature* **1962**, *195*, 68. (b) Etter, M. C.; Panunto, T. W. *J. Am. Chem. Soc.* **1988**, *110*, 5896 and references cited therein.