

Synthesis and structure of the first propeller-shaped helical coordination polymer $\{ [Ag(S,S)\text{-bis(oxazoline)}] (\text{OTf}) \}_\infty$

MA, Sheng-Ming* (麻生明) WU, Shu-Lin (吴树林)

Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

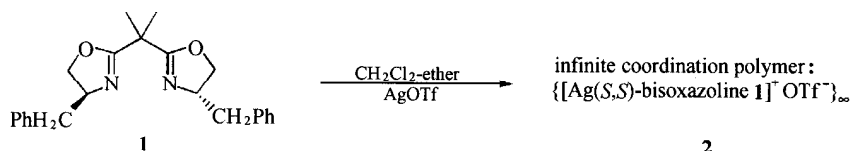
A mixture of (*S,S*)-bis(oxazoline) ligand (**1**) with silver trifluoromethane sulfonate afforded a helical coordination polymer (**2**). Its structure was determined by X-ray single-crystal diffraction.

Keywords Bis(oxazoline) ligand, helical coordination polymer, crystal structure

Recently much attention has been paid to the application of optically active bis(oxazoline) ligands in asymmetric catalysis.¹ Utilization of Ag^+ salts as well as their complexes as a catalyst in organic transformation, such as cyclization of 1,2-allenyl ketone to furans,² cyclization of 1,2-allenyl carboxylic acids to butenolides,³ cyclization of allenyl carbinols to 2,5-dihydrofurans,⁴ the

asymmetric cyclization reaction of isocyanoacetic acid or isocyanomethane toluenesulfonate with aldehydes,⁵ asymmetric intramolecular carbene-C-H insertion reaction,⁶ and enantioselective addition of allylic tin reagents to aldehydes⁷ has been becoming a new focus. During the course of our study on the new methodologies for the stereoselective synthesis of butenolides,⁸ we were interested in the coordination chemistry between Ag^+ and the well-recognized chiral ligand bis(oxazoline)s to form chiral complexes, which may show enantioselectivity in organic transformation.

To a solution of (*S,S*)-bisoxazoline (**1**)⁹ in CH_2Cl_2 was added silver trifluoromethanesulfonate in ether. The mixture was stirred at room temperature for 1.5 h to give the white solid **2**.¹⁰



¹H NMR data in CD_3CN solution were considerably different from those of the free ligand in the same solvent (Table 1). Notable differences are that one of OCH_2 signals has been thoroughly overlapped with that of the NCH proton and an apparent ABX splitting pattern for the $\text{C}_6\text{H}_5\text{CH}_2$ protons in the free ligand has changed to an AX spin system in the complex, indicating that the benzylic protons in **2** are equivalent. This spectrum also revealed the presence of only one kind of oxazoline moi-

ety, demonstrating equivalence of the two heterocycles caused either by symmetry or flexibility.

X-ray diffraction study of the single crystal of **2**¹¹ clearly showed that it was an infinitely single-stranded helical coordination polymer¹² with twofold symmetry and left-handed helicity (Figs. 1, 2, and 3). Coordinated by two nitrogen atoms of two adjacent ligands, the Ag^+ ion is not sited on the screw axis. It is interesting to note that its space-layout viewed from *b* axis is just like

Received December 2, 1999; accepted February 18, 2000.

Project supported by the National Natural Science Foundation of China (No. 29525202), Chinese Academy of Sciences, and Shanghai Municipal Committee of Science and Technology (No. 98QA14001).

a propeller (Fig. 3), and perfect stacking of the carbon-nitrogen bonds and phenyl rings were also observed. Two other coordination complexes¹³ of similarly structured ligands (*S,S*)-2,6-bis(4'-benzyl-oxazolin-2'-yl)pyridine and (*R,R*)-bis(4'-phenyloxazolin-2'-yl)-pyri-

dine with AgBF_4 have been reported, however, only double $[\text{Ag}_2((S,S)\text{-}2,6\text{-bis}(4'\text{-benzyloxazolin-}2'\text{-yl)pyridine)}_2]^{2+}$ or triple helicates $[\text{Ag}_3((R,R)\text{-bis}(4'\text{-phenyloxazolin-}2'\text{-yl)pyridine)}_3]^{3+}$ were afforded.

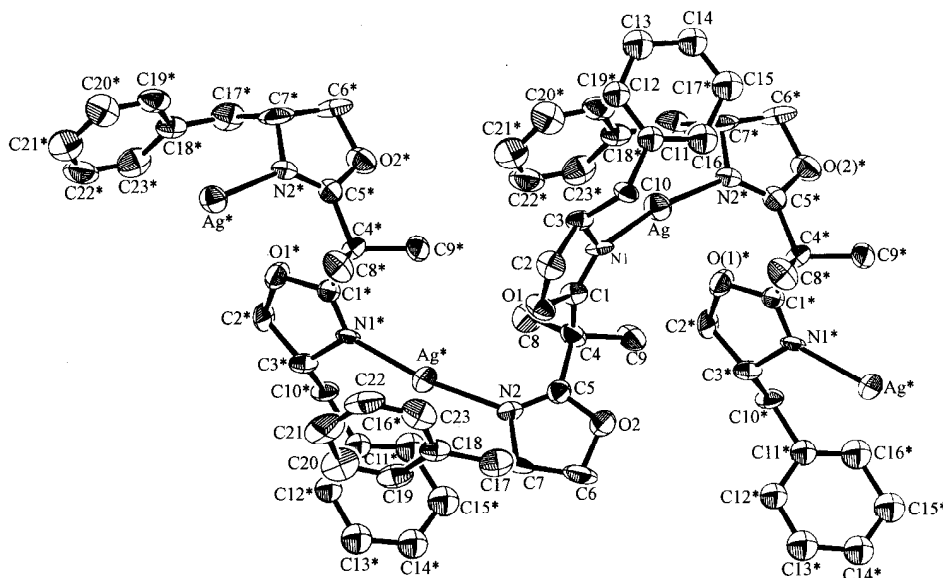


Fig. 1 ORTEP drawing of the coordination environment in 2.

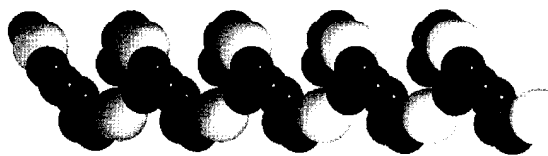


Fig. 2 Space-filling diagram of the helical chain in 2 with all the substituent omitted for clarity.

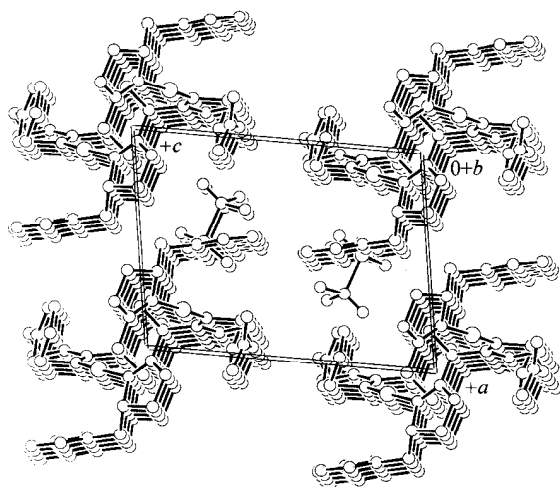


Fig. 3 Molecular packing of 2 viewed along the *b* axis.

With regard to the structural parameters, the bond angle of $\text{N}(1)\text{-Ag-N}(2)$ is $169.7(3)^\circ$, slightly deviating from the perfect linear geometry. The bond lengths of $\text{Ag-N}(1)$ and $\text{Ag-N}(2)$ are $0.2156(10)$ and $0.216(1)$ nm, typical for two-coordinating Ag(I) .¹² The shortest distance between Ag and oxygen atom of O1f^- is 0.519 nm, which reveals that the triflate counterion is fully dissociated from the metal center, a phenomenon which is important for enhancing ionic conductivity.¹⁴

In conclusion, we have prepared the first infinite helical coordination polymer of Ag^+ with a bisoxazoline ligand. The study of its catalytic activity is being carried out in our laboratory.

References and notes

- For a most recent review, see: Ghosh, A. K.; Mathivanan, P.; Cappiello, J., *Tetrahedron: Asymmetry*, **9**, 1 (1998).
- a) Marshall, J. A.; Robinson, E. D., *J. Org. Chem.*, **55**, 3450(1990).
b) Marshall, J. A.; Wang, X.-J., *J. Org. Chem.*, **56**, 960(1991).
c) Marshall, J. A.; Wallace E. M., *J. Org. Chem.*,

- 60, 796(1995).
3. Marshall, J. A.; Wolf, M. A.; Wallace, E. M., *J. Org. Chem.*, **62**, 367(1997).
 4. a) Marshall, J. A.; Pinney, K. G., *J. Org. Chem.*, **58**, 7180(1993).
b) Marshall, J. A.; Schon, C. A., *J. Org. Chem.*, **60**, 5966(1995).
c) Marshall, J. A.; Yu, R. H.; Perkins, J. F., *J. Org. Chem.*, **60**, 5550(1995).
 5. a) Hayashi, T.; Uozumi, Y.; Yamazaki, A., *Tetrahedron Lett.*, **32**, 2799(1991).
b) Sawamura, M.; Hamashima, H.; Ito, Y., *J. Org. Chem.*, **55**, 5935(1990).
 6. Burgess, K.; Lim, H.-J.; Porte, A. M.; Sulikowski, G. A., *Angew. Chem. Int. Ed. Engl.*, **35**, 220(1996).
 7. a) Yanagisawa, A.; Nakashima, H.; Ishiba, A.; Yamamoto, H., *J. Am. Chem. Soc.*, **118**, 4723(1996).
b) Yanagisawa, A.; Ishiba, A.; Yamamoto, H., *Synlett.*, 88(1997).
c) Yanagisawa, A.; Matsumoto, Y.; Nakashima, H.; Asakawa, K.; Yamamoto, H., *J. Am. Chem. Soc.*, **119**, 9319(1997).
d) Yanagisawa, A.; Nakatsuka, Y.; Nakashima, H.; Yamamoto, H., *Synlett.*, 9331(1997).
 8. a) Ma, S.; Shi, Z., *J. Org. Chem.*, **63**, 6387(1998).
b) Ma, S.; Shi, Z.; Yu, Z., *Tetrahedron Lett.*, **40**, 2393(1999).
c) Ma, S.; Shi, Z.; Yu, Z., *Tetrahedron*, **55**, 12137(1999).
d) Ma, S.; Wu, S., *J. Org. Chem.*, **64**, 9314(1999).
 9. Complex **1** was prepared according to the known method: Matt, P. Von; Lloyd-Jones, G. C.; Minidis, A. B. E.; Pfaltz, A.; Macko, L.; Neuburger, M.; Zehnder, M.; Ruegger, H.; Pregosin P. S., *Helv. Chim. Acta*, **78**, 265(1995).
 10. For complex **2**: mp $\geq 160^\circ\text{C}$ (decomposed), $[\alpha]_{\text{D}}^{20} = -31.0^\circ$ (*c* 1.7, CH_3CN) or $[\Phi]_{\text{D}}^{20} = -191.9^\circ$. δ_{H} (300 MHz, CD_3CN): 7.38—7.28(m, 10H, $2\text{C}_6\text{H}_5$), 4.51—4.39(m, 4H, 2CHN, 2CH-O), 4.18—4.13(A of ABX, $J_{\text{AB}} = 7.8$ Hz, $J_{\text{AX}} = 6.2$ Hz, 2H, 2CH-O), 2.92—2.89(d, $J = 6.2$ Hz, 4H, $2\text{CH}_2\text{Ph}$), 1.46(s, 6H, 2CH_3). For ligand **1**: $[\alpha]_{\text{D}}^{20} = -90.9^\circ$ (*c* 1.0, CH_3CN) or $[\Phi]_{\text{D}}^{20} = -329.1^\circ$. δ_{H} (300 MHz, CD_3CN): 7.35—7.26(m, 10H, $2\text{C}_6\text{H}_5$), 4.42—4.32(m, 2H, 2CH-N), 4.25—4.19, 4.01—3.96(AB of ABX, $J_{\text{AB}} = 9.3$ Hz, $J_{\text{AX}} = 8.4$ Hz, $J_{\text{BX}} = 6.9$ Hz, 4H, $2\text{CH}_2\text{O}$), 2.94—2.87, 2.79—2.73(AB of ABX, $J_{\text{AB}} = 12.0$ Hz, $J_{\text{AX}} = 6.3$ Hz, $J_{\text{BX}} = 6.8$ Hz, 4H, $2\text{CH}_2\text{Ph}$), 1.39(s, 6H, 2CH_3).
 11. Single crystals suitable for X-ray diffraction analysis were obtained from acetonitrile by diffusion of diethyl ether into the solution at room temperature. X-ray crystal data for **2**: ($\text{C}_{24}\text{H}_{26}\text{O}_5\text{N}_2\text{AgSF}_3$)_n, $M_r = 619.40 \times n$, Colorless prismatic, Space group $P2_1$ (#4), $a = 0.9417(3)$, $b = 1.1007(3)$, $c = 1.2204(2)$ nm, $\beta = 98.31(2)^\circ$, $V = 1.251(1)$ nm³, $Z = 2$, $D_c = 1.643$ g/cm³, $F(000) = 628.00$. Rigaku AFC7R diffractometer, $\mu(\text{Mo K}\alpha) = 9.47$ cm⁻¹, $\lambda = 0.071069$ nm, ω - 2θ scan, $T = 293$ K. The final cycle of full matrix least-square refinement was based on $1931(I) > 2.50\sigma(I)$ observed reflections and 306 variable parameters, and converged with unweighted and weighted agreement factors of $R = 0.054$ and $R_w = 0.069$, respectively.
 12. For the formation of infinite Ag^+ -bidenate ligand complex, see:
 - a) Aakeroy, C. B.; Beatty, A. R., *Chem Commun.*, 1067(1998).
 - b) Wu, B.; Zhang, W.; Yu, S.; Wu, X., *J. Chem. Soc., Dalton Trans.*, 1795(1997).
 - c) Bowyer, P. K.; Porter, K. A.; Rae, A. D.; Willis, A. C.; Wild, S. B., *Chem. Commun.*, 1153(1998).
 - d) Constable, E. C.; Kulke, T.; Neuburger, M.; Zehnder, M., *Chem. Commun.*, 489(1997).
 - e) Suzuki, T.; Kotsuki, H.; Isobe, K.; Moriya, N.; Nakagawa, Y.; Ochi, M., *Inorg. Chem.*, **34**, 530(1995).
 - f) Tong, M.; Chen, X.; Ye, B.; Ng, S. W., *Inorg. Chem.*, **37**, 5278(1998).
 For the complexes of Ag^+ with multidenate ligands, see: Modder, J. F.; Kotten, G. Van; Vrieze, K.; Spek, A. L., *Angew. Chem. Int. Ed. Engl.*, **28**, 1698(1989).
 13. Provent, C.; Hewage, S.; Brand, G.; Bernardinelli, G.; Charbonniere, L.; Williams, J. A. F., *Angew. Chem. Int. Ed. Engl.*, **36**, 1287(1997).
 14. MacGlashan, G. S.; Andreev, Y. G.; Bruce, P. G., *Nature*, **389**, 792(1999).