Synthesis and structural characterization of infinite single-stranded coordination polymers of optically active bis(oxazoline) ligands with silver trifluoromethanesulfonate

Shengming Ma* and Shulin Wu

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, P. R. China.
E-mail: masm@pub.sioc.ac.cn

Received (in New Haven, CT, USA) 16th April 2001, Accepted 29th May 2001
First published as an Advance Article on the web 7th September 2001

Three novel complexes, [Ag(*S*,*S*-**1**)][CF_3SO_3] (**3**), [Ag(*S*,*S*-**2**)][CF_3SO_3] · 0.5H_2O (**4**) and [Ag(*R*,*R*-**2**)][CF_3SO_3] · 0.5H_2O (**5**) [**1** = 2,2-bis(4′-benzyloxazolin-2′-yl)propane, **2** = 2,2-bis(4′-phenyloxazolin-2′-yl)propane] were obtained from silver trifluoromethanesulfonate and the corresponding bis(oxazoline) ligands. The crystal structures of compounds **3** and **4** were determined by X-ray diffraction. The subtle difference in the substitution at the 4-position of the oxazoline ring in the ligands led to a remarkable change in the structures of complexes **3** and **4**. Complex **3** is an infinite single-stranded helical coordination polymer with two-fold symmetry and left-handed helicity, while complexe **4** is an infinite single-stranded polymer with zig-zag conformation. However, the extended structures are not maintained in solution, undergoing rapid ligand redistribution and rapid dynamic exchange among several nonequivalent species as determined by ESMS spectra.

The design and construction of metal coordination polymers is currently of interest due to their potential applications in materials science,[1] supramolecular chemistry[2] and catalytic processes.[3,4] One recently highlighted topic in this area is concerned with chiral and helical assemblies, which are not only the object of molecular architecture, but also used as asymmetric catalysts.[5] For this reason, in a preliminary communication,[6] we have examined the synthesis and X-ray crystallography of a non-racemic helical polymer {[Ag(*S*,*S*)-bis(oxazoline)](OTf)}$_\infty$. The use of bis(oxazolines)[7] presents advantages over other nitrogen-containing ligands in that they are easily prepared, both enantiomers being readily available from optically pure amino alcohols. Furthermore, optically active oxazoline-ligated metal complexes may possess desirable catalytic properties with high enantioselectivity. On the other hand, among d^{10} metals helical coordination polymers have been mostly observed with silver(I) complexes.[8] Utilization of Ag^+ salts as well as their complexes as catalysts in organic transformations, such as cyclization of 1,2-allene derivatives,[9] the asymmetric cyclization reaction of isocyanoacetic acid or isocyanomethane toluenesulfonate with aldehydes,[10] asymmetric intramolecular carbene C–H insertion reactions,[11] and enantioselective addition of allylic tin reagents to aldehydes,[12] has become a new focus. In this paper, we report the full details of the synthesis and structural characterization of the optically active helical polymer {[Ag(*S*,*S*)-bis(oxazoline)](OTf)}$_\infty$, **3**. As an extension to this work, two other chiral coordination polymers of Ag(I) with bis(oxazoline) ligands, **4** and **5**, have also been synthesized and structurally characterized.

Experimental

^{1}H NMR spectra were recorded on Bruker AM 300 or 400 spectrometers using $CDCl_3$ or CD_3CN as the solvent. Electrospray MS (ESMS) spectra were recorded on a Perkin-Emer Mariner LC-MS spectrometer; the sample was loaded using acetonitrile as the solvent. Silver trifluoromethanesulfonate was prepared by the reaction of trifluoromethanesulfonic acid and silver carbonate;[13] the bis(oxazoline) ligands *S*,*S*-(−)-**1**,[14] *S*,*S*-(−)-**2** and *R*,*R*-(+)-**2**[15] were prepared according to the literature methods, that is by the treatment of dimethylmalonyl chloride with the corresponding amino alcohols, followed by dehydrative cyclization.

Synthesis

[Ag(*S*,*S*-1)][CF_3SO_3] (3). To a solution of *S*,*S*-(−)-**1** (36.1 mg, 0.1 mmol) in CH_2Cl_2 (20 mL) was added a solution of silver trifluoromethanesulfonate (25.7 mg, 0.1 mmol) in diethyl ether (10 mL). The mixture was stirred at room temperature to gradually afford a white precipitate. After 1.5 h, the white solid (54.0 mg, 87.2%) was collected by filtration and washed with diethyl ether. Mp ⩾ 160 °C (dec). ^{1}H NMR (400 MHz, CD_3CN): δ 1.76 (s, 6H), 3.20–3.22 (d, J = 6.2, 4H), 4.46–4.48 (dd, J = 7.8, 6.2 Hz, 2H), 4.73–4.78 (m, 4H), 7.58–7.69 (m, 10H). ESMS: *m*/*z* (%) 469.1 (100.00), 471.1 (93.58). Anal. calc. for $C_{24}H_{26}AgF_3N_2O_5S$: C 46.53, H 4.23, N 4.52; found C 46.31, H 4.35, N 4.44%.

[Ag(*S*,*S*-2)][CF_3SO_3] · 0.5H_2O (4). To a solution of *S*,*S*-(−)-**2** (33.4 mg, 0.1 mmol) in CH_2Cl_2 (20 mL) was added a solution of silver trifluoromethanesulfonate (25.7 mg, 0.1 mmol) in diethyl ether (10 mL). The mixture was stirred at room temperature for 1.5 h and the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (5 mL) and filtered. The filtrate was treated with hexane (15 mL) to give the product as white solids, 43.5 mg (72.5%). Mp 208 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.59 (s, 6H), 4.23 (t, J = 8.2, 2H), 4.86 (t, J = 9.6, 2H), 5.17–5.42 (dd, J = 7.9, 2.3 Hz, 2H), 7.11–7.14 (m, 4H), 7.25–7.35 (m, 6H). ESMS: *m*/*z* (%) 441.1 (100.00), 443.1 (96.84), 775.3 (74.08), 777.2 (54.77). Anal. calc. for $C_{44}H_{46}Ag_2F_6N_4O_{11}S_2$: C 44.01, H 3.86, N 4.67; found C 44.10, H 4.01, N 4.80%.

[Ag(*R*,*R*-2)][CF_3SO_3] · 0.5H_2O (5). Complex **5** was prepared as for complex **4**. *R*,*R*-(−)-**2** (33.4 mg, 0.1 mmol) and silver trifluoromethanesulfonate (25.7 mg, 0.1 mmol) gave 41.3

mg of the white solid product (68.2%). Mp 208 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.61 (s, 6H), 4.23 (t, $J = 8.2$, 2H), 4.86 (t, $J = 9.5$, 2H), 5.40 (dd, $J = 7.6$, 2.7 Hz, 2H), 7.11–7.14 (m, 4H), 7.25–7.34 (m, 6H). ESMS: m/z (%) 441.1 (99.74), 443.1 (93.67), 775.3 (95.80), 777.3 (100.00). Anal. calc. for $C_{44}H_{46}Ag_2F_6N_4O_{11}S_2$: C 44.01, H 3.86, N 4.67; found C 43.80, H 3.89, N 4.59%.

X-Ray crystallography

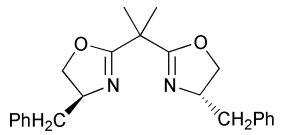
Single crystals of **3** were obtained *via* diffusion of diethyl ether into its CH_3CN solution while single crystals of **4** were obtained *via* diffusion of hexane into its CH_2Cl_2 solution. Crystals both with approximate dimensions of $0.20 \times 0.20 \times 0.30$ mm^3 were chosen and mounted on glass fibres. All measurements were made on a Rigaku AFC 7R diffractometer with graphite monochromated Mo-Kα ($\lambda = 0.710\,69$ Å) radiation. Diffraction intensities were collected at 20.0 °C using the $\omega - 2\theta$ technique.

The structures were solved by direct methods and expanded using Fourier techniques. Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Some hydrogen atoms were refined isotropically, the rest were included in fixed positions. Neutral atom scattering factors were taken from ref. 16. Calculations were performed using TEXSAN.[17] The crystallographic data for both complexes are listed in Table 1.

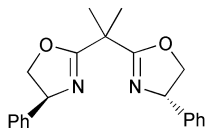
CCDC reference numbers 166479 and 166480. See http://www.rsc.org/suppdata/nj/b1/b103402m/ for crystallographic data in CIF or other electronic format.

Results and discussion

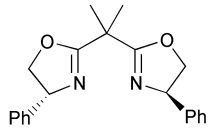
The optically pure bis(oxazoline) ligands (*S*,*S*)-**1**, (*S*,*S*)-**2** and (*R*,*R*)-**2** were easily prepared from the corresponding amino alcohols and dimethylmalonyl chloride.[14,15] The corresponding reactions with AgO_3SCF_3 (1 : 1 metal-to-ligand ratio) in CH_2Cl_2–diethyl ether at room temperature afforded complexes **3**, **4** and **5**, respectively, as white solids. They have the chemical formulae [Ag(*S*,*S*-**1**)][CF_3SO_3], [Ag(*S*,*S*-**2**)][CF_3SO_3]$\cdot 0.5H_2O$ and [Ag(*R*,*R*-**2**)][CF_3SO_3]$\cdot 0.5H_2O$, respectively. The water molecules probably came either from the solvent or from air. Complex **3** is both air-stable and light-stable in the solid state, and insoluble in common organic solvents such as diethyl ether, THF, acetone, ethanol, CH_2Cl_2 and $CHCl_3$ and readily soluble in CH_3CN; but complexes **4** and **5** are light-sensitive and easily dissolved in CH_2Cl_2, $CHCl_3$ and CH_3CN. These different properties suggest that they probably have different structures in the solid state. From the single crystal X-ray analysis described below, the Ag(I) compound **3** is shown to be a helical polymer while **4** only forms zig-zag chains in the solid state. The ^{1}H NMR spectra reveal that all of them are present as monomeric species in solution.



S,*S*-**1**



S,*S*-**2**



R,*R*-**2**

Single crystal X-ray structural analysis

The crystal structure of **3** is shown in Fig. 1 and 2. It has an infinite single-stranded helical structure consisting of Ag(I) atoms and the bridging ligands. The Ag^+ ions, coordinated by two nitrogen atoms of two adjacent ligands, are not sited on the screw axis, but symmetrically arranged on two sides of it. Perfect stackings of the oxazoline and phenyl rings were also observed. With regard to the structural parameters, the bond angle N(1)–Ag–N(2) is 169.7(3)°, slightly deviating from perfect linear geometry. The torsion angles N(1)–C(1)–O(1)–C(2) and O(1)–C(1)–N(1)–C(3) are 8(1) and 4(1)° respectively, demonstrating that the oxazoline ring displays a twisted conformation. The bond lengths of Ag–N(1) and Ag–N(2) are 2.156(1) and 2.16(10) Å, typical for a two-fold coordinated Ag(I).[8,19] The shortest distance between Ag and the oxygen atoms of OTf^- is 5.19 Å, which reveals that the triflate counterion is fully dissociated from the metal center.

Recently, two other coordination complexes[18] of similarly structured ligands (*S*,*S*)-2,6-bis(4-benzyloxazolin-2-yl)pyridine and (*R*,*R*)-bis(4-phenyloxazolin-2-yl)pyridine, with $AgBF_4$ have been reported, however, only *non-infinite double* $[Ag_2\{(S,S)\text{-2,6-bis(4-benzyloxazolin-2-yl)pyridine}\}_2]^{2+}$ or *triple* $[Ag_3\{(R,R)\text{-bis(4-phenyloxazolin-2-yl)pyridine}\}_3]^{3+}$ helicates were obtained. Hence, compound **3** is the first example of a helical coordination polymer from Ag(I) and

Table 1 Summary of crystal data of complexes **3** and **4**

	3	**4**
Chemical formula	$C_{24}H_{26}O_5N_2AgSF_3$	$C_{44}H_{42}O_{11}N_4Ag_2S_2F_6$
Formula weight	619.40	1196.68
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$ (no. 4)	$P2_1$ (no. 4)
a/Å	9.417(3)	14.684(4)
b/Å	11.007(3)	10.869(3)
c/Å	12.204(2)	16.467(6)
β/°	98.31(2)	109.14(2)
U/Å^3	1251(1)	2483(1)
Z	2	2
T/°C	20.0	20.0
μ(Mo-Kα)/mm^{-1}	94.7	95.3
Total reflections	4598	4639
Unique reflections	4299	4451
R_{int}	0.025	0.055
Obs. reflections	1931 [$I > 2.50\sigma(I)$]	3160 [$I > 3.00\sigma(I)$]
Residuals: R, R_w[a]	0.054; 0.069	0.057; 0.069

[a] $R = \Sigma\|\|F_o| - |F_c\|/\Sigma|F_o|$, $R_w = [\Sigma_w(|F_o| - |F_c|)^2/\Sigma_w|F_o|^2]^{1/2}$, $w = 4F_o/\sigma^2(F_o)^2$.

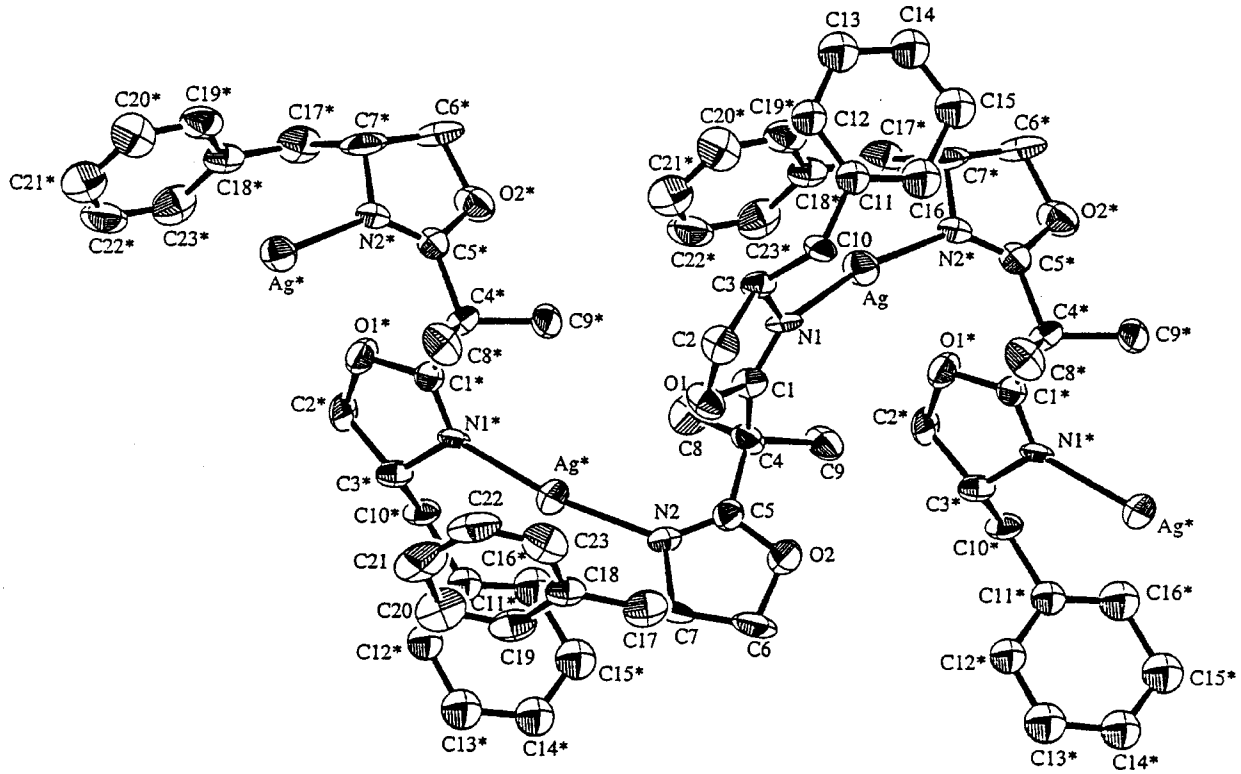


Fig. 1 ORTEP drawing of the coordination environment in complex **3** with thermal ellipsoids at 30%. Ag–N(1) = 2.156(10), Ag–N(2) = 2.16(1) Å; N(1)–Ag–N(2) = 169.7(3)°.

bis(oxazoline) ligands. It is noteworthy that complex **3** is also one of the few non-racemic helical polymers[19] structurally characterized.

The crystal structure of **4**[20] (Fig. 3 and 4) is also an infinite single-stranded polymer consisting of Ag(I) atoms and bis(oxazoline) bridges. However, no helical conformations were found; only zig-zag chains with a periodicity of two Ag^+ ions and two ligand molecules were formed. As in **3**, each Ag^+ ion is ligated by two nitrogen atoms belonged to two ligands. All Ag^+ ions are located on a non-crystallographic axis parallel to the *a* axis. The triflate counterion is fully dissociated from the metal center, as in the case of complex **3**. The interstices are occupied by water molecules, which have no direct interaction with the polymer chains, forming weak hydrogen bonds with the triflates.

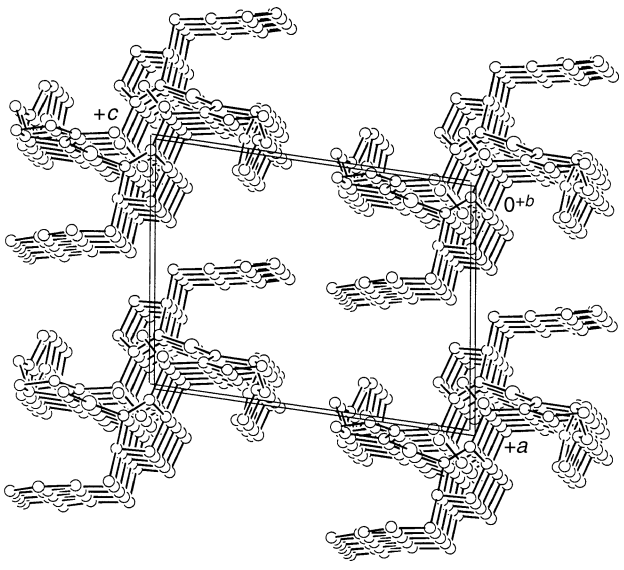


Fig. 2 Molecular packing of complex **3** viewed along the *b* axis.

In the periodic fragment of **4** (Fig. 3), two nonequivalent Ag^+ ions are identified. Ag(1) is coordinated by two nitrogen atoms in a linear fashion with a N(1)–Ag(1)–N(2) bond angle of 177.6(4)°, while Ag(2) displays a distorted linear coordination geometry with N(3)–Ag(2)–N(4) equal to 158.4(4)°. Ag–N distances range from 2.12(1) to 2.18(1) Å.

It is clear that the drastic change in the structures of **3** and **4** results from the subtle difference in the substitution at the 4-position of the oxazoline ring in the ligands. The phenomenon that diverse conformations can be achieved by subtle changes in the nature of the constituent groups has also been found in related Ag^+ complexes.[18] In our examples, the benzyl group at the 4-position of oxazoline makes ligand **1** more flexible than ligand **2**. In a sense, helical conformations can be achieved by using flexible ligands.[21]

^{1}H NMR and ESMS study in solution

The ^{1}H NMR data of **3** in CD_3CN solution are somewhat different from those of the free ligand in the same solvent.[6] Notable differences are that one of the OCH_2 signals in complex **3** is thoroughly overlapped with that of the NCH proton and an apparent ABX splitting pattern for the $C_6H_5CH_2$ protons in the free ligand has changed to an AX spin system in the complex. This spectrum also revealed the presence of only one kind of oxazoline moiety, demonstrating the equivalence of the two heterocycles, probably caused by fluctionality based on rapid cleavage and re-formation of the Ag–N bond. Electrospray (ES) mass spectrometry of **3** in CH_3CN solution only shows a pair of peaks at *m*/*z* 469.1 and 471.1, which can be assigned to monomeric **1**-$^{107}Ag^+$ and **1**-$^{109}Ag^+$.

^{1}H NMR spectra of **4** and **5** in $CDCl_3$ solution show six sets of peaks, which are virtually the same as those of the free ligands[15] in the same solvent and also show the presence of only one kind of oxazoline moiety. Electrospray (ES) mass spectra of **4** and **5** in CH_3CN solution show peaks at *m*/*z* 441.1 (**2**-$^{107}Ag^+$) and 443.1 (**2**-$^{109}Ag^+$). However, another set of peaks at *m*/*z* 775.3 and 777.3 suggests that $[(\mathbf{2})_2\text{-Ag}]^+$ is present. Thus, it is concluded that the extended structures are

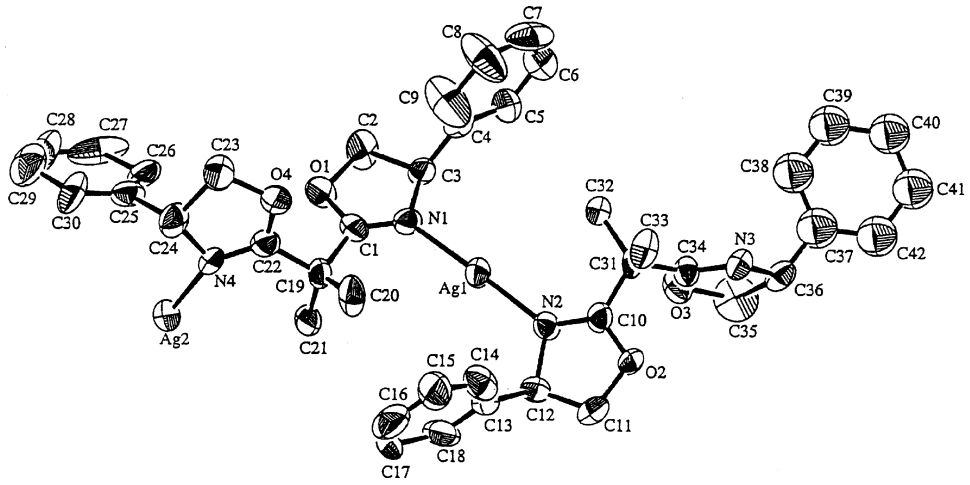


Fig. 3 ORTEP drawing of the coordination environment in complex **4** with thermal ellipsoids drawn at 30%. Ag(1)–N(1) = 2.12(1), Ag(1)–N(2) = 2.16(1), Ag(2)–N(3) = 2.18(1), Ag(2)–N(4) = 2.16(1) Å; N(1)–Ag(1)–N(2) = 177.6(4), N(3)–Ag(2)–N(4) = 158.4(4)°.

not maintained in solution and undergo rapid ligand redistribution and rapid dynamic exchange among several nonequivalent species.

Conclusion

Three novel coordination polymers **3**, **4** and **5** have been prepared from silver trifluoromethanesulfonate and the corresponding optically active bis(oxazoline) ligands (*S*,*S*)-**1**, (*S*,*S*)-**2** and (*R*,*R*)-**2**. All three complexes consist of infinite single-stranded chains in the solid state. Complex **3** is a helical coordination polymer with left-handed helicity, while complexes **4** and **5** are polymers with zig-zag conformations. The subtle difference in the substitution at the 4-position of the oxazoline ring in the ligands led to a remarkable change in the structures of complexes **3** and **4**. Helical conformation can be achieved by using flexible ligands. All three extended structures are not maintained in solution, undergoing rapid ligand redistribution and rapid dynamic exchange among several nonequivalent species.

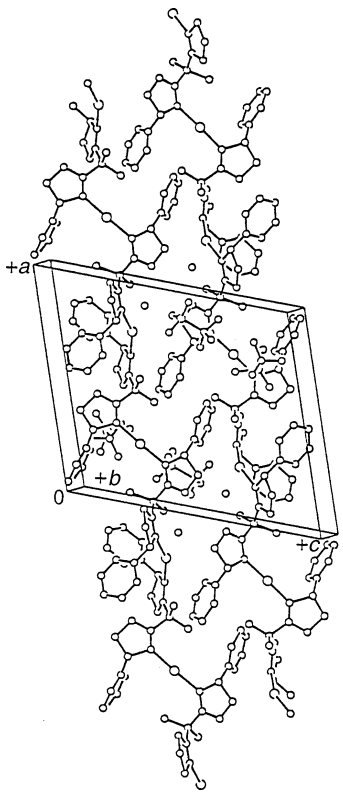


Fig. 4 The cell unit for complex **4**.

Acknowledgements

We thank the Major State Basic Research Development Program (grant no. G2000077500), Chinese Academy of Sciences, Shanghai Municipal Committee of Science and Technology and Postdoctoral Foundation of Shanghai for financial support. S. M. is the recipient of the 1999 Qiu Shi Award for Young Scientific Workers issued by the Hong Kong Qiu Shi Foundation of Science and Technology (1999–2003).

References and notes

1 (*a*) G. S. MacGlashan, Y. G. Andreev and P. G. Bruce, *Nature* (*London*), 1999, **389**, 792; (*b*) O. Kahn and C. J. Martinez, *Science*, 1998, **279**, 44; (*c*) R. Robson, in *Comprehensive Supramolecular Chemistry*, ed. D. D. MacNicol, F. Toda and R. Bishop, Pergamon, Oxford, 1996, vol. 6, p. 733; (*d*) S. Subramanian and M. J. Zaworotko, *Coord. Chem. Rev.*, 1994, **137**, 357; (*e*) C.-T. Chen and K. S. Suslick, *Coord. Chem. Rev.*, 1993, **128**, 293; (*f*) J. S. Miller, A. J. Epstein and W. M. Reiff, *Acc. Chem. Res.*, 1988, **21**, 114.

2 R. Robson, B. M. Abraham, S. R. Batten, R. W. Gable, B. F. Hoskins and J. Liu, *Supramolecular Architecture*, ed. T. Bein, ACS Symp. Ser. 499, American Chemical Society, Washington, DC, 1992, p. 256.

3 T. J. Barton, M. L. Bull, W. G. Klemperer, D. A. Loy, B. McEaney, M. Mosono, P. A. Mosono, G. Pez, G. W. Scherer, J. C. Vartuli and O. M. Yaghi, *Chem. Mater.*, 1999, **11**, 263.

4 (*a*) D. Hagrman, C. Zubieta, D. J. Rose, J. Zubieta and R. C. Haushalter, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 873; (*b*) O. M. Yaghi and H. Li, *J. Am. Chem. Soc.*, 1995, **117**, 10401; (*c*) B. F. Abraham, B. F. Hoskins, B. M. Michail and R. Robson, *Nature* (*London*), 1994, **369**, 727; (*d*) M. Fujita, Y. J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151; (*e*) L. R. MacGillivray, S. Subramanian and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1994, 1325.

5 (*a*) E. J. Corey, C. L. Cymin and M. C. Noe, *Tetrahedron Lett.*, 1994, **35**, 69; (*b*) K. Maruoka, N. Murase and H. Yamamoto, *J. Org. Chem.*, 1993, **58**, 2938.

6 S. Ma and S. Wu, *Chin. J. Chem.*, 2000, **18**, 444.

7 For a recent review, see: A. K. Ghosh, P. Mathivanan and J. Cappiello, *Tetrahedron: Asymmetry*, 1998, **9**, 1.

8 (*a*) K. Nomiya, R. Noguchi and M. Oda, *Inorg. Chim. Acta*, 2000, **298**, 32, and references cited therein; (*b*) C. B. Aakeroey and A. R. Beatty, *Chem Commun.*, 1998, 1067; (*c*) E. C. Constable, T. Kulke, M. Neuburger and M. Zehnder, *Chem. Commun.*, 1997, 489.

9 (*a*) J. A. Marshall and E. D. Robinson, *J. Org. Chem.*, 1990, **55**, 3450; (*b*) J. A. Marshall and X.-J. Wang, *J. Org. Chem.*, 1991, **56**, 960; (*c*) J. A. Marshall and E. M. Wallace, *J. Org. Chem.*, 1995,

60, 796; (*d*) J. A. Marshall, M. A. Wolf and E. M. Wallace, *J. Org. Chem.*, 1997, **62**, 367; (*e*) J. A. Marshall and K. G. Pinney, *J. Org. Chem.*, 1993, **58**, 7180; (*f*) J. A. Marshall and C. A. Sehon, *J. Org. Chem.*, 1995, **60**, 5966; (*g*) J. A. Marshall, R. H. Yu and J. F. Perkins, *J. Org. Chem.*, 1995, **60**, 5550.

10 (*a*) T. Hayashi, Y. Uozumi, A. Yamazaki, M. Sawamura, H. Hamashima and Y. Ito, *Tetrahedron Lett.*, 1991, **32**, 2799; (*b*) M. Sawamura, H. Hamashima and Y. Ito, *J. Org. Chem.*, 1990, **55**, 5935.

11 K. Burgess, H.-J. Lim, A. M. Porte and G. A. Sulikowski, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 220.

12 (*a*) A. Yanagisawa, H. Nakashima, A. Ishiba and H. Yamamoto, *J. Am. Chem. Soc.*, 1996, **118**, 4723; (*b*) A. Yanagisawa, A. Ishiba and H. Yamamoto, *Synlett.*, 1997, 88; (*c*) A. Yanagisawa, Y. Matsumoto, H. Nakashima, K. Asakawa and H. Yamamoto, *J. Am. Chem. Soc.*, 1997, **119**, 9319; (*d*) A. Yanagisawa, Y. Nakatsuka, H. Nakashima and H. Yamamoto, *Synlett.*, 1997, 933.

13 G. M. Whitesides and F. D. Gutowski, *J. Org. Chem.*, 1976, **41**, 2882.

14 P. von Matt, G. C. Lloyd-Jones, A. B. E. Minidis, A. Pfaltz, L. Macko, M. Neuburger, M. Zehnder, H. Ruegger and P. S. Pregosin, *Helv. Chim. Acta*, 1995, **78**, 265.

15 E. J. Corey, N. Imai and H. Zhang, *J. Am. Chem. Soc.*, 1991, **113**, 728.

16 D. T. Cromer and J. T. Waber, *International Tables for Crystallography*, Kynoch Press, Birmingham, 1974, vol. IV, Table 2.2 A.

17 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1985 and 1992.

18 C. Provent, S. Hewage, G. Brand, G. Bernardinelli, L. J. Charbonniere and A. F. Williams, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1287.

19 (*a*) P. K. Bowyer, K. A. Porter, A. D. Rae, A. C. Willis and S. B. Wild, *Chem. Commun.*, 1998, 1153; (*b*) B. Wu, W.-J. Zhang, S.-Y. Yu and X.-T. Wu, *J. Chem. Soc., Dalton Trans.*, 1997, 1795; (*c*) T. Suzuki, H. Kotsuki, K. Isobe, N. Moriya, Y. Nakagawa and M. Ochi, *Inorg. Chem.*, 1995, **34**, 530.

20 A structural determination of **5** carried out showed the structure to be enantiomorphous to structure **4**, but the crystallographic data is too poor to report here.

21 M. Hong, W. Su, R. Cao, M. Fujita and J. Lu, *Chem. Eur. J.*, 2000, **6**, 427.