Self-assembly of Homochiral Double Helix and Side-by-side Helix Conformers of a Double-stranded Disilver(I)–Tetra(tertiary phosphine) Complex

Anthea L. Airey, Gerhard F. Swiegers, Anthony C. Willis and S. Bruce Wild*

Research School of Chemistry, Institute of Advanced Studies, Australian National University, Canberra ACT 0200, Australia

Optically pure (S,S)-(+)-Ph$_2$PCH$_2$CH$_2$P(Ph)CH$_2$CH$_2$P(Ph)CH$_2$CH$_2$PPh$_2$, (S,S)-1, spontaneously self-assembles into left-handed double-stranded D_2-double helix and C_2-side-by-side helix conformers of the disilver(I) cation; the crystal and molecular structure of Λ-(−)-[Ag$_2${(R,R)-1}$_2$][PF$_6$]$_2$ is reported.

The self-assembly of molecular components into unique supramolecular helical structures is a feature of biology that can now be mimicked by a variety of inorganic coordination complexes. Thus, the spontaneous synthesis of double- or triple-stranded polynuclear metal helices[1] (and molecular links and knots[2]) from semi-rigid oligo-2,2'-bipyridines and related ligands has aroused considerable interest from the point of view of molecular architecture and also because of the implications for biology. In general, the double-stranded metal helices (also termed double-stranded helicates[3]) have been prepared from achiral ligands and isolated as racemic mixtures or as conglomerates (separated in one instance[4]) with little work being directed towards the stereoselective synthesis of polynuclear helices from homochiral ligands. In an investigation related to the generation of artificial ion channels, however, diastereoisomeric diiron(III) helices were generated from a triple-stranded tripodal ligand containing L-leucine amide and hydroxamate groups, which acted as ligands and hydrogen-bonding groups, respectively.[5] In other work, tricopper(I) and trisilver(I) double helices were synthesised from appropriate metal salts and a tris(2,2-bipyridine) ligand containing a pair of homochiral α-methyl-2-pyridylmethanol spacer groups; circular dichroism measurements indicated 95% helical induction in the complex by the homochiral ligand.[6] Recently the resolution of a triple-stranded dicobalt(III) helix was achieved by elution of the racemate on a column of Sephadex SP-C25 ion exchange resin with sodium antimonyl-D-tartrate.[7]

To date, linear poly(tertiary phosphines), which are usually isolated as mixtures of diastereoisomers because of the configurational stability of the pyramidal inner-phosphorus stereocentres (E_{inv} ca. 130 kJ mol^{-1}),[8] do not appear to have been investigated as potential ligands for the synthesis of polynuclear metal helices. For the stereoselective synthesis of a poly(tertiary phosphine)-di- or -oligo-metal helix, however, the homochiral forms of the ligands will be required and such compounds have not been available until recently.[9] In earlier work, we showed that tetrahedral bis(bidentate)silver(I) complexes of bis(tertiary phosphines) are kinetically labile and rearrange into equilibrium mixtures of diastereoisomers in appropriate cases.[10] Thus, silver(I) in conjunction with the homochiral form of a linear tetra(tertiary phosphine) appeared to be an ideal combination for the spontaneous assembly of a double-stranded disilver double helix. Energy minimisation calculations[11] indicated that the tetra(tertiary phosphine) Ph$_2$PCH$_2$CH$_2$P(Ph)CH$_2$CH$_2$P(Ph)CH$_2$CH$_2$PPh$_2$[12] in homochiral form would produce double-stranded double helix and side-by-side helix disilver(I) cations of similar energies. Here we report the synthesis of Λ-(−)-[Ag$_2${(R,R)-1}$_2$][PF$_6$]$_2$, which crystallises in the space group $P1$ with one molecule each of the D_2-double helix and C_2-side-by-side helix conformers of the disilver cation and associated anions in each unit cell. It is noteworthy that 2,6-bis(1-methylbenzimidazol-2-yl)pyridine and 1,3-bis(1-methylbenzimidazol-2-yl)benzene react with copper(I) to produce double helix and non-helical side-by-side dicopper complexes, respectively, the structures of which are maintained in each case in polar aprotic solvents.[13]

Thus silver(I) perchlorate, when treated with an equimolar quantity of (S,S)-(+)-1 in methanol, followed by the addition of

a twofold excess of ammonium hexafluorophosphate in the same solvent, affords (−)-[Ag$_2${(R,R)-1}$_2$][PF$_6$]$_2$ as colourless needles in 92% yield, mp 194–195 °C.†‡ Recrystallisation of this material from hot methanol gave prisms of the pure complex suitable for single-crystal structural analysis. Conductivity data for Λ-(−)-[Ag$_2${(R,R)-1}$_2$][PF$_6$]$_2$ in acetonitrile at 21 °C over the concentration range 10^{-2}–10^{-4} mol dm^{-3} gave a slope A of 794 Ω^{-1} equiv.$^{-3/2}$ cm^2 l$^{1/2}$ for the Onsager law $\Lambda_e = \Lambda_o - AC_e^{\frac{1}{2}}$, which compares with calculated values of 890 and 334 Ω^{-1} equiv.$^{-3/2}$ cm^2 l$^{1/2}$ in this solvent for typical 2 : 1 and 1 : 1 electrolytes, respectively.[15]

The structure determination of (−)-[Ag$_2${(R,R)-1}$_2$][PF$_6$]$_2$ revealed both double helix and side-by-side helix conformers of the disilver cations in the unit cell (Fig. 1).§ The binding of the

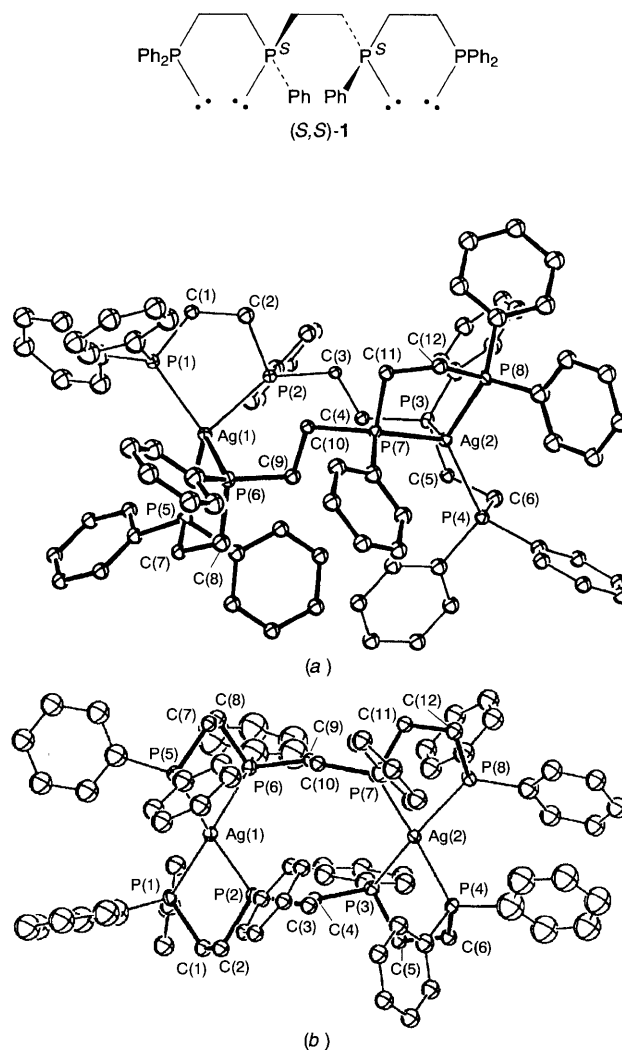(S,S)-1

(a)

(b)

Fig. 1 ORTEP plots of the double-stranded double helix (a) and side-by-side helix (b) conformers of Λ-(−)-[Ag$_2${(R,R)-1}$_2$][PF$_6$]$_2$

ligands to the silver ions is completely stereoselective in each of the conformational diastereoisomers of the complex giving silver stereocentres of (S) configuration. The essential difference between the two structures lies in the relationship between the helicities of the central ten-membered rings, which have the twist–boat–chair–boat (TBCB) conformation rather than the usual achiral BCB conformation of cyclodecane and its derivatives,[16] and the configurations of the chiral inner-phosphorus stereocentres: when the ten-membered ring has the λ conformation, the phenyl groups attached to the inner phosphorus stereocentres of (R) configuration adopt equatorial dispositions and the axial terminal diphenylphosphinoethyl groups are in position to generate the D_2-double helix conformation of the complex; when the central ring has the δ conformation, the terminal diphenylphosphinoethyl groups have equatorial dispositions, which results in the tighter turns of the side-by-side helix conformation of the complex (Fig. 2). The difference between the two conformations of the complex is accordingly reflected in the C–C–P–C torsion angles running from the central carbon–carbon bonds of the ten-membered rings through to the adjacent phosphorus–carbon bonds of the terminal five-membered rings. In the double helix conformer of idealised D_2-symmetry [torsion angles 176–178°, Ag$\cdots$Ag 6.859(3) Å], each molecule of the tetra(tertiary phosphine) completes one half-turn of a left-handed or Λ helix (as does the overall complex); in the side-by-side conformer of idealised C_2-symmetry [torsion angles 63–80°, Ag$\cdots$Ag 6.072(4) Å], each of the ligands completes one and one-half turns of a Λ helix. The unique side-by-side helical arrangement of the poly(tertiary phosphines) about the silver ions is the structural motif of the leucine repeat or zipper transcriptional regulatory proteins, wherein two polypeptide α-helices are held together by
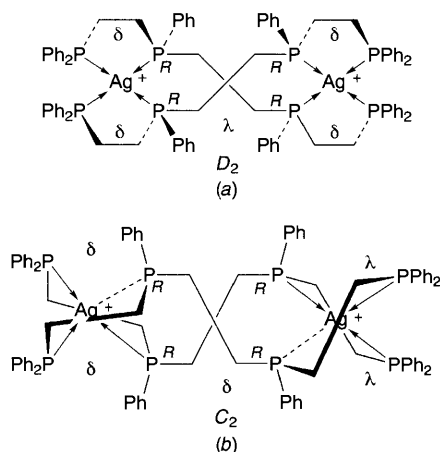

Fig. 2 Schematic side-elevations of the double-stranded D_2-double helix (a) and C_2-side-by-side helix (b) conformers of Λ-(−)-[Ag$_2${(R,R)-1}$_2$][PF$_6$]$_2$
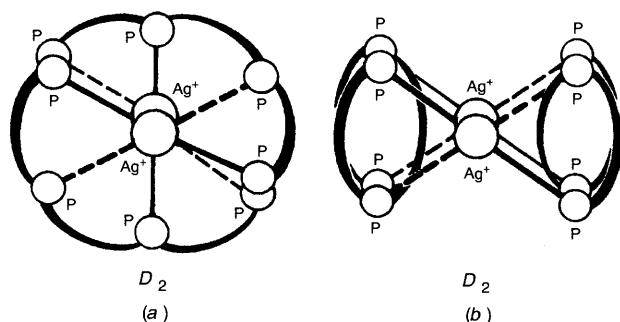

Fig. 3 Schematic end-elevations of the double-stranded D_2-double helix (a) and D_2-side-by-side helix (b) conformers of Λ-(−)-[Ag$_2${(R,R)-1}$_2$][PF$_6$]$_2$

hydrogen bonding in a parallel side-by-side arrangement.[17] For each of the central ten-membered ring conformations, λ or δ, there are seven different combinations of the four terminal five-membered-ring conformations lying between the idealised D_2-double helix (central ring λ, terminal rings $\delta,\delta,\delta,\delta$) and the idealised D_2-side-by-side helix (central ring δ, terminal rings $\lambda,\lambda,\lambda,\lambda$) (Fig. 3). Energy minimisation calculations indicate remarkably similar energies for all fourteen structures with the persistence of the observed chiral conformation of the central ten-membered ring; moreover, the λ conformation of this ring always generated double helix structures and the δ conformation side-by-side helix structures with the (R)-tetra(tertiary phosphine).

Footnotes

† Selected spectroscopic data for Λ-(−)-[Ag$_2${(R,R)-1}$_2$][PF$_6$]$_2$: [α]$_D^{21}$ −7.5 (c 1.0, CH$_2$Cl$_2$). ^{31}P NMR (CD$_2$Cl$_2$): δ 5.67, 3.63, 131.24, 137.12, 142.34, 148.82, 154.65. Correct elemental analyses were obtained.

‡ The coordination of the phosphine to the metal is stereospecific with retention of configuration at phosphorus: the apparent inversion is a consequence of the Cahn–Ingold–Prelog (CIP) rules for assigning absolute configurations.[14]

§ Crystal data for Λ-(−)-[Ag$_2${(R,R)-1}$_2$][PF$_6$]$_2$: C$_{84}$H$_{84}$Ag$_2$F$_{12}$P$_{10}$, M_r = 1847.06, colourless prisms from methanol, space group $P1$, a = 12.420(4), b = 12.641(4), c = 27.270(9) Å, α = 92.59(3), β = 94.82(3), γ = 99.15(3)°; U = 4204(2) Å^3; D_c = 1.459 g cm^{-3} for Z = 2; F(000) = 1880; μ(Mo-Kα) = 7.2 cm^{-1}; Philips PW 1100/20 diffractometer (20 °C); ω–2θ scan method. A total of 10999 data were collected in the range 4 < 2θ < 45° of which 6123 [I > 3σ(I)] were refined. The structure was solved by heavy-atom and difference-Fourier techniques. The absolute configuration was assigned on the basis of the known chirality of the ligand. Subsequent refinement (full-matrix least squares, phenyl rings as rigid bodies) afforded R and R_w values of 0.070 and 0.066, respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 J.-M. Lehn, Angew. Chem., Int. Ed. Engl., 1990, 29, 1304; E. C. Constable, Tetrahedron, 1992, 48, 10013.
2 C. Dietrich-Buchecker and J.-P. Sauvage, Bull. Soc. Chim. Fr., 1992, 129, 113.
3 J.-M. Lehn, A. Rigault, J. Siegel, J. Harrowfield, B. Chevrier and D. Moras, Proc. Natl. Acad. Sci. USA, 1987, 84, 2565.
4 R. Kramer, J.-M. Lehn, A. De Cian and J. Fischer, Angew. Chem., Int. Ed. Engl., 1993, 32, 703.
5 J. Libman, Y. Tor and A. Stanzer, J. Am. Chem. Soc., 1987, 109, 5880.
6 W. Zarges, J. Hall, J.-M. Lehn and C. Bolm, Helv. Chim. Acta, 1991, 74, 1843.
7 L. J. Charbonniere, G. Bernardinelli, C. Piguet, A. M. Sargeson and A. F. Williams, J. Chem. Soc., Chem. Commun., 1994, 1419.
8 K. Mislow, Trans. N.Y. Acad. Sci., 1973, 35, 227.
9 A. L. Airey, G. F. Swiegers, A. C. Willis and S. B. Wild, preceding paper.
10 G. Salem, A. Schier and S. B. Wild, Inorg. Chem., 1987, 27, 3029.
11 Energy minimisation calculations were performed by using the program SPARTAN 3.0 in conjunction with the force-field program TRIPOS 5.2 (Wavefunction Inc., Irvine, CA, 1992) with additional metal parameters from SPARTAN.
12 R. B. King and P. N. Kapoor, J. Am. Chem. Soc., 1971, 93, 4158.
13 C. Piguet, G. Bernardinelli and A. F. Williams, Inorg. Chem., 1989, 28, 2920; S. Ruttiman, C. Piguet, G. Bernardinelli, B. Bocquet and A. F. Williams, J. Am. Chem. Soc., 1992, 114, 4230.
14 R. S. Cahn, C. K. Ingold and V. Prelog, Angew. Chem., Int. Ed. Engl., 1966, 5, 385.
15 R. D. Feltham and R. G. Hayter, J. Chem. Soc., 1964, 4587; R. K. Burgess and D. A. Zakko, J. Chem. Educ., 1975, 52, 649 and references cited therein.
16 J. B. Hendrickson, J. Am. Chem. Soc., 1967, 89, 7047; E. Engler, J. D. Andose and P. von R. Schleyer, J. Am. Chem. Soc., 1973, 95, 8005.
17 E. K. O'Shea, R. Rutkowski and P. S. Kim, Science, 1989, 243, 538.