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Synthesis and structure of a helical polymer $[Ag(R,R\text{-DIOP})(NO_3)]_n$ {DIOP = (4*R*,5*R*)-*trans*-4,5-bis[(diphenylphosphino)methyl]-2,2-dimethyl-1,3-dioxalane}

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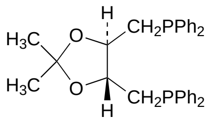
A polymeric complex of silver(I) with the chiral ligand (*R*,*R*)-DIOP {DIOP = (4*R*,5*R*)-*trans*-4,5-bis[(diphenylphosphino)methyl]-2,2-dimethyl-1,3-dioxalane} has been synthesized; its crystal structure revealed that the complex had a right-handed helical extended structure and consists of a silver atom co-ordinated by two phosphorus atoms of two adjacent (*R*,*R*)-DIOP ligands and an oxygen atom of nitrate.

Helicity and chirality[1] are interesting topics within the fields of chemistry, biochemistry and materials science and considerable attention has focused on the design and construction of metal complexes with helical conformations (*i.e.* helicates[2]). This type of complex has potential application to some newly emerging fields, such as supramolecular chemistry,[3] asymmetric catalysis[4] and non-linear optical materials.[5] A number of helicates have been synthesized,[6] but few optically active pure ones have been reported.[7] Here we report the synthesis and characterization of a helical polymer of silver(I) with the chiral ligand (*R*,*R*)-DIOP {DIOP = (4*R*,5*R*)-*trans*-4,5-bis[(diphenylphosphino)methyl]-2,2-dimethyl-1,3-dioxalane} which is an important bidentate phosphine ligand. The metal complexes of the ligand have been well described as catalysts in a variety of asymmetric reactions.[8]

Treatment of the optically pure DIOP witn an equimolar amount of $AgNO_3$ in methanol yields a colourless transparent solution from which a white powder † was isolated by mixing with diethyl ether. Colourless crystals suitable for X-ray analysis were obtained by recrystallization of the powder from methanol.



(R,R)-DIOP

The complex has an extended structure ‡ as shown in Fig. 1. It consists of a Ag atom co-ordinated by two phosphorus atoms of two adjacent ligands and an oxygen atom of nitrate. The Ag–P(1) distance of one ligand is 2.411(2) Å and the Ag–P(2a) distance of a neighbouring ligand is 2.403(2) Å. The Ag–P distances (average 2.402 Å) are in the region of those for $[Ag_4(dpm)_4(NO_3)_2]^{2+}$ (dpm is an achiral bidentate phosphine) (average 2.401 Å).[12] The Ag–O(1) distance [2.530(7) Å] is slightly longer than that in the latter (average 2.510 Å). A slightly distorted plane is composed of the four atoms Ag, P(1), P(2a) and O(1). The angles P(1)–Ag–P(2a), P(1)–Ag–O(1) and P(2a)–Ag–O(1) are 148.49(8), 106.2(2) and 105.0(2)°, respectively. There is a two-fold screw axis parallel to the crystallographic *b* axis in the polymer (see Fig. 2). The polymer chain consists of silver atoms and the ligands extend along the screw axis in a right-handed helix. The Ag · · · Ag(a) distance is 8.358 Å and that of Ag · · · Ag(a′), along the helical axis, is 16.186 Å. The O · · · O(1) distance (2.760 Å) shows that there is a hydrogen bond between the solvent CH_3OH and the NO_3^- anion.

Although a variety of transition-metal complexes with the ligand (*R*,*R*)-DIOP have been reported, most of them were single metal complexes with *cis*-bidentate co-ordination,[13] however, a binuclear copper complex bridged by an aryl derivative of DIOP[8] has been obtained.

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† To optically pure DIOP (0.50 g, 1.0 mmol), prepared from L-tartaric acid according to the literature,[9] in dried methanol (30 cm^3) was added $AgNO_3$ (0.17 g, 1.0 mmol). After refluxing under an Ar atmosphere in the dark for about 1 h, the mixture was filtered and the filtrate concentrated to about 5 cm^3. To this dried diethyl ether (20 cm^3) was added which led to the formation of a white powder (0.52 g, yield 74%) (Found: C, 54.79; H, 5.05. Calc. for $C_{32}H_{36}AgNO_6P_2$: C, 54.82; H, 5.14%). ^1H NMR (CD_3OD, 499.887 MHz): δ 7.780 and 7.375 (two groups, m, 20 H, C_6H_5), 4.093 (t, 2 H, CH), 2.462 (d, 4 H, CH_2), 1.301 (s, 6 H, CH_3). ^{31}P-{^1H} NMR (CD_3OD, 202.361 MHz): δ 28.911 [d, J(Ag–P) = 205 Hz].

‡ Crystal data for $[Ag(R,R\text{-DIOP})(NO_3)]_n$: $[C_{32}H_{36}AgNO_6P_2]_n$, $M_r = 700.46 \times n$, orthorhombic, space group $P212121$ (no. 19), $a = 11.486(5)$, $b = 16.186(5)$, $c = 17.754(9)$ Å, $U = 3300.6(24)$ Å^3, $T = 293(2)$ K, $Z = 4$, $D_c = 1.408$ Mg cm^{-3}, $\lambda = 0.710\,73$ Å, μ(Mo-Kα) = 0.750 cm^{-1}, $F(000) = 1436$, colourless prism with dimensions 0.25 × 0.20 × 0.18 mm. Data were collected on a Siemens SMART CCD area-detector diffractometer, and corrected for absorption by SADABS.[10] The range of absorption factors is 1.0000 to 0.6767. A total of 1261 frames were collected with a graphite monochromator in a three-circle goniometer (fixed *x*). The exposure time of a frame was 10 s. Data collection range $3.40 < 2\theta < 46.54$, $-11 \leqslant h \leqslant 12$, $-17 \leqslant k \leqslant 16$, $-19 \leqslant l \leqslant 15$. Final R value on $[I > 4\sigma(I)]$ data was 0.0493. 13 128 Reflections measured, 4733 unique ($R_{int} = 0.0619$, $R_\sigma = 0.0828$) which were used in all calculations. The absolute configuration was confirmed by an x refinement: $x = 0.021(39)$. All calculations were performed on a INDY workstation using the SHELXL 93 program package.[11] Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/516.

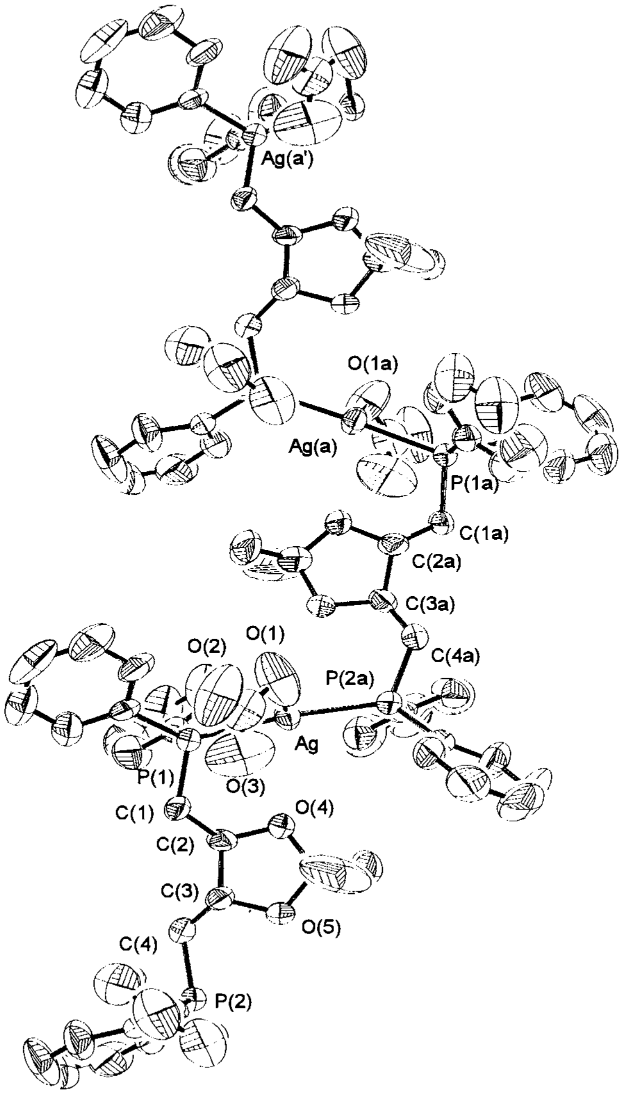

Fig. 1 Perspective drawing of the helically extended array in [Ag{(*R*,*R*)-DIOP}(NO$_3$)]*n* along the crystallographic *b* axis

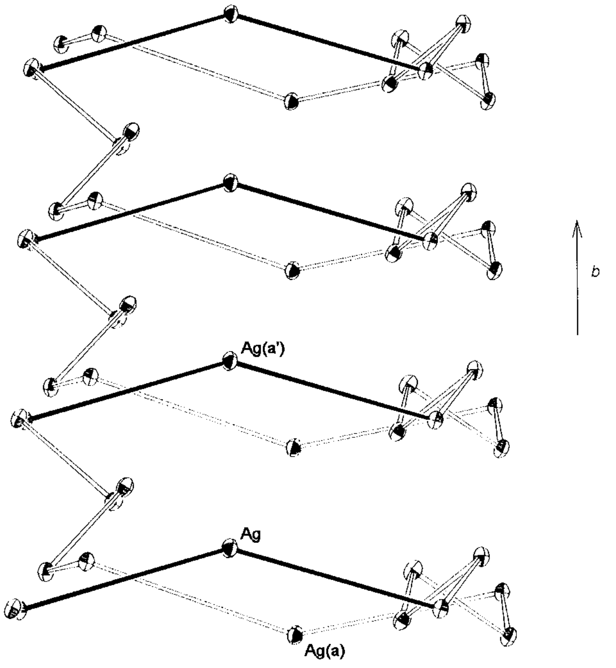

Fig. 2 The structure along the *b* axis. Some C, O, N and H atoms are omitted for clarity

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