From helicate to infinite coordination polymer: crystal and molecular structures of silver(I) complexes of readily prepared di-Schiff bases

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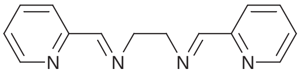
The readily prepared di-Schiff base of pyridine-2-aldehyde and ethane-1,2-diamine 1 reacts with silver(I) tetrafluoroborate to form by self-assembly the double-stranded D_2-helicate (±)-[$Ag_2$1$_2$](BF_4)$_2$; the corresponding Schiff base of (1*R*,2*R*)-cyclohexane-1,2-diamine [(*R*,*R*)-2] reacts with silver(I) nitrate to produce the homochiral single-stranded C_2-coordination polymer *M*-{[Ag{(*R*,*R*)-2}]NO_3·$2H_2O$}$_\infty$.

Double- and triple-stranded helicates are generated when metals combine with ligands containing appropriate metallophilic and helicating elements. Thus, the bis(methylene)oxy group inserted between a pair of semi-rigid 2,2′-bipyridines destabilises single-stranded mononuclear metal chelates of univalent Group 11 ions, but facilitates the self-assembly of double-stranded dinuclear metal helicates.[1,2] Moreover, a homochiral helicating element in the ligand can induce considerable stereoselectivity in the product.[3] There is now available a wide variety of structural motifs for the self-assembly of double- and triple-stranded helicates, many of which are derived from ligands having as their metallophilic elements familiar chelating entities, including 2,2′-bi- and oligo-pyridines and related compounds,[4] and a tetra(tertiary phosphine).[5] Herein we report the syntheses and crystal and molecular structures of silver(I) complexes of the readily prepared di-Schiff bases **1**[6] and (*R*,*R*)-**2**,[7] *viz.* the double-stranded helicate (±)-[Ag_2**1**$_2$](BF_4)$_2$ and the infinite single-stranded coordination polymer *M*-{[Ag{(*R*,*R*)-**2**}]NO_3·$2H_2O$}$_\infty$. The crystal and molecular structures of the related double-stranded helicate (±)-[Ag_2{(*R*,*S*)-**2**}$_2$](CF_3SO_3)$_2$ have been determined previously[8] and detailed NMR spectroscopic investigations of this compound and the parent (±)-[Ag_2**1**$_2$](CF_3SO_3)$_2$ have indicated that both helicates have two-fold symmetry in solution.[8,9] In other work, it has been shown that silver(I) combines with a single enantiomer of a bis(pyridyl) ligand derived from L- or D-tartaric acid to give an extended single- stranded helicate, whereas the corresponding racemic form of the ligand produces a disilver(I) complex incorporating both enantiomers in a *meso* arrangement.[10]



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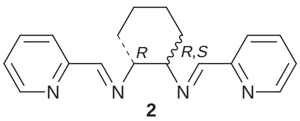

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The complex (±)-[Ag_2**1**$_2$](BF_4)$_2$ was isolated as pale-yellow prisms from acetonitrile–diethyl ether, mp 221–221.5 °C (decomp.).‡ The ^{1}H NMR spectrum of the complex in [$^2H_3$]acetonitrile is consistent with the presence of a pair of homotopic ligands[2] and the electrospray MS of the complex at a cone potential of 25 V displays a pattern of peaks in the range *m*/*z* 776–783 due to [Ag_2**1**$_2$·BF_4]$^+$. The salt crystallises as a racemic compound in the orthorhombic space group $C222_1$ (no. 20) with four pseudo inversion related pairs of cations and associated anions in the unit cell [Fig. 1(*a*)].§ Each disilver(I) cation has D_2 symmetry with the two homotopic ligands spanning both silver(I) ions. The Ag···Ag distance in the cation is 3.024 Å (av.). The overall structure can be described as a modulation of an idealised *Fddd* parent structure in which true inversion relates two substructures of *F*222 symmetry with *C*-centred layers of the different substructures interleaved perpendicular to ***c***. Within a layer, the dimeric cation occupies a site of 222 symmetry with the anions located on two-fold rotation axes parallel to ***b*** at 1/2, ± 0.15, 0 from the cation. The modulation lowers the symmetry of the structure from *Fddd* to $C222_1$ (a subgroup of *Fddd*) and destroys the crystallographic symmetry relationships between the substructures, which now also have $C222_1$ symmetry. The modulation displaces layers of one substructure along ***a*** and displaces layers of the other substructure along ***b***, while retaining a pseudo inversion between adjacent layers. Layers of the first substructure contain two-fold rotation axes parallel to ***a*** that relate adjacent layers of the second substructure and layers of the second substructure contain two-fold rotations parallel to ***b*** that relate adjacent layers of the first substructure. The asymmetric unit for the space group $C222_1$ contains two quarters of a dimeric cation and one anion from the first substructure and two quarters of a dimeric cation and two half anions from the second sub-

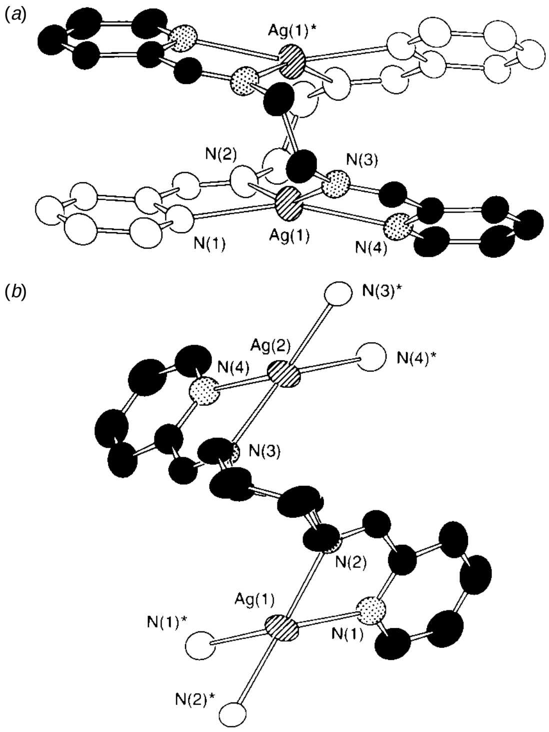

Fig. 1 Molecular structures of double-stranded helical cation of (±)-[Ag_2**1**$_2$](BF_4)$_2$ (*a*) and of repeating unit of cation of single-stranded *M*-{[Ag{(*R*,*R*)-**2**}]NO_3·$2H_2O$}$_\infty$ (*b*)

structure. It was not necessary to invoke disorder in the structure.

The complex M-$\{[\mathrm{Ag}\{(R,R)\text{-}\mathbf{2}\}]\mathrm{NO_3{\cdot}2H_2O}\}_\infty$ crystallises as amber plates from acetonitrile–diethyl ether in the hexagonal space group $P6_522$. The polynuclear metal cation of the complex is an infinite helical polymer of C_2 symmetry with each interlocking $\mathrm{Ag_2N_4}$ unit completing 0.73 turns of a left-handed (M) helix [Fig. 1(*b*)]. The pitch of the single-stranded palindromic helix is 6.5 Å and the Ag···Ag distances are 5.42 Å (av.). Each tetrahedral silver ion in the helix has the *S* configuration. Parallel helical chains form layers perpendicular to ***c*** with the 6_5 screw axis of $P6_522$ relating adjacent layers to give an overall structure of *M* helicity. The reference layer at $z = 1/4$ propogates parallel to ***a***, inducing pseudorotation axes midway between the real rotation axes (Fig. 2). The pseudosymmetry of the structure allows the possibility of homometric solutions, a translation of 1/2 ***b*** relating alternative positions for the polymer chain that produces the same intensities should the 1/2 ***a*** translation hold exactly. The ligands enclose N(terminal)–Ag–Ag–N(terminal) angles of 190.5° (av.), implying an average pitch of 7.3 Å for the $\mathrm{Ag_2N_4}$ helical core. Comparative refinement allowed the absolute structure to be determined. The ^{1}H NMR spectrum in [^{2}H$_3$]acetonitrile and the electrospray MS of the complex are consistent with disproportionation of the polymer into dinuclear metal helicates in solution. The helical displacements in the helicate and the helicalpolymer are evident in the space-filling diagram given in Fig. 3. Fig. 1 shows the *ob* and *lel* arrangements of the central carbon–carbon bonds in the two structures. The crystal molecular structures of two other single-stranded helicate polymers derived from achiral ligands have been described previously.[11,12] To our knowledge, however, the only other homochiral co-ordination polymer to be structurally characterised is the complex P-$\{\mathrm{Ag}[(R,R)\text{-DIOP}]\mathrm{NO_3}\}_n$ {DIOP = (4*R*,5*R*)-*trans*-4,5-bis[(diphenylphosphino)methyl]-2,3-dimethyl-1,3-dioxalane} in which each silver ion in the polymer is coordinated by two phosphorus atoms of adjacent (*R*,*R*)-DIOP ligands and a nitrate-*O* atom.[13]

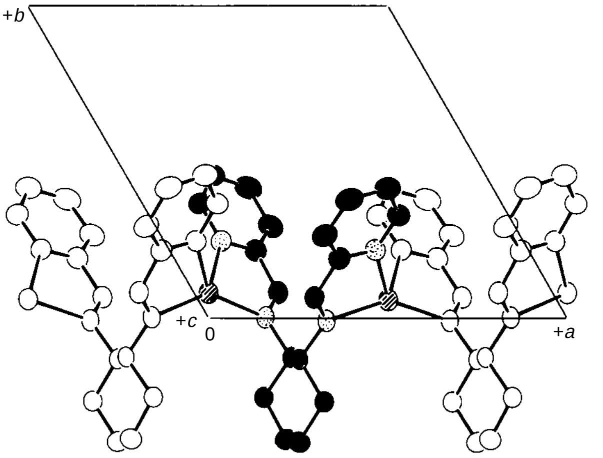

Fig. 2 Cation of M-$\{[\mathrm{Ag}\{(R,R)\text{-}\mathbf{2}\}]\mathrm{NO_3{\cdot}2H_2O}\}_\infty$ at $z = 1/4$

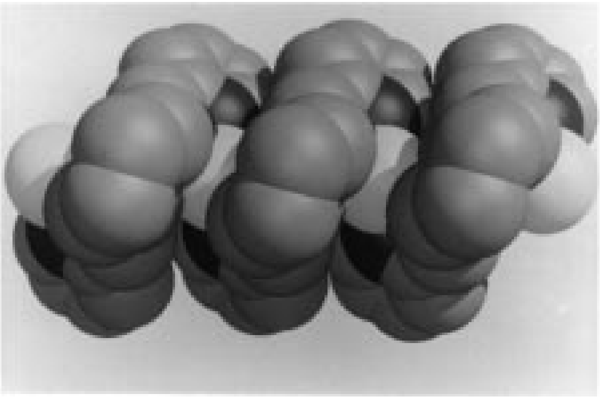

Fig. 3 Space-filling diagram of cation of M-$\{[\mathrm{Ag}\{(R,R)\text{-}\mathbf{2}\}]\mathrm{NO_3{\cdot}2H_2O}\}_\infty$ with hydrogen atoms omitted

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Notes and References

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‡ Satisfactory elemental analyses were obtained.

§ *Crystal data* for (±)-$[\mathrm{Ag_2}\mathbf{1}_2](\mathrm{BF_4})_2$: $\mathrm{C_{28}H_{28}Ag_2B_2F_8N_8}$, M_r 865.93, pale yellow block, space group $C222_1$ (no. 20), $a = 10.420(2)$, $b = 25.036(7)$, $c = 25.202(7)$ Å, $U = 6573(3)$ Å^3, $Z = 8$; $D_\mathrm{c} = 1.749$ g cm^{-3}, μ(Mo-Kα) = 12.67 cm^{-1}. Philips PW1100/ 20 diffractometer; $T = 293$ K, ω–2θ scan method. A total of 4176 unique data were collected in the range $5 \leqslant 2\theta \leqslant 55°$ of which 1650 [$I > 3\sigma(I)$] were used for the refinement. Initial unconstrained refinement of the data gave an R value of 0.060, but spreads in equivalent bond lengths were as high as 0.2 Å, which indicated refinement difficulties associated with the pseudo-inversion centre relating adjacent layers of the structure. Subsequent constrained refinement using the program RAELS96 (A. D. Rae, Australian National University, Canberra, Australia) with use of 176 independent parameters to describe the 53 anisotropic non-hydrogen atoms in the structure gave R and R_w values of 0.048 and 0.059, respectively, with a uniform distribution of error over all data classes. M-$\{[\mathrm{Ag}\{(R,R)\text{-}\mathbf{2}\}]\mathrm{NO_3{\cdot}2H_2O}\}_\infty$: $\mathrm{C_{18}H_{28}AgN_5O_7}$, M_r 498.29, pale yellow hexagonal plate, space group $P6_522$ (no. 179), $a = b = 10.876(4)$, $c = 63.522(8)$ Å, $U = 6507(4)$ Å^3, $Z = 12$; $D_\mathrm{c} = 1.526$ g cm^{-3}, μ(Cu-Kα) = 77.78 cm^{-1}. Rigaku AFC6R diffractometer; $T = 296$ K, ω scan method. A total of 2067 independent reflections having $2\theta \leqslant 120°$ were measured. Constrained refinement (RAELS96) with use of 109 variables to describe the 31 non-hydrogen atoms in the asymmetric unit and their anisotropic thermal motion gave R and R_w values of 0.072 and 0.101, respectively, for 1026 reflections with [$I > 3\sigma(I)$] for a poorly diffracting thin plate. The homometrically related structure refined to an R value of 0.15. Refinement in $P6_122$ gives the incorrect helicity for the ligand and produces worse refinement statistics. CCDC 182/843.

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