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Self-assembly of silver(I) polymers with single strand double-helical structures containing the ligand *O*,*O*′-bis(8-quinolyl)-1,8-dioxaoctane

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The flexible multidentate ligand *O*,*O*′-bis(8-quinolyl)-1,8-dioxaoctane (ODOQ) reacted with AgX (X = ClO_4^-, BF_4^-, $CF_3SO_3^-$, or $CF_3CO_2^-$) to give four new complexes $[Ag(ODOQ)]_nX_n$: X = ClO_4^- **1**; X = BF_4^- **2**; X = $CF_3SO_3^-$ **3**, and $[Ag(ODOQ)(CF_3CO_2)]_n$ **4**. All four complexes have been characterized by elemental analyses, IR and ^1H NMR spectroscopy. Single crystal X-ray analyses showed that they have similar 1-D extended architectures with each ligand in "~" shape, while the chains are alternately and parallelly arranged with the silver(I) atoms as the backbone to form double helical mesomeric strands. The structures are controlled more by the spacer $(CH_2)_6$ than by the anions: the versatile coordination geometry of the silver(I) atom is trigonally bonded but changes to distorted tetrahedral or trigonal bipyrimidal *via* weak Ag···O interactions. In addition, face-to-face π···π (in **1**–**4**) and edge-to-face C–H···π (in **3**) interactions as well as hydrogen bonds C–H···O and C–H···F between adjacent strands assemble the cations in **1**–**3** or neutral molecules in **4** into an extended network.

Introduction

Supramolecular architectures, especially those displaying helical character, have particular relevance to biological systems and asymmetric catalysis[1] and have attracted much attention in recent years. Helicates may be obtained from the combination of metal ions with flexible chain-ligands containing bidentate subunits such as 2,2′-bipyridyl groups connected by covalent bridges[2] or terpyridine and its derivatives with conformational freedom.[3] In a sense, these ligands still have some rigidity, because of their relatively short subunit-to-subunit length. When such achiral ligands are used, inherent chiral helicates are generally formed as racemic mixtures.[4] Introduction of flexible spacers between two bulky bis-bidentate subunits has been reported to give helical structures.[4] Therefore, it would be interesting to introduce longer spacer chains and find out the helicity of the complexes formed.

The field of helicates has recently been reviewed by Piguet,[5a] and a few cases of infinite coordination helices have been reported. Most of these are racemates of P (or Δ) and M (or Λ) helices,[2c,5–7] while a few lead to mesomers with both Δ- and Λ-helices within one single infinite chain.[8] In the meantime, most reported complexes usually contain double or triple stranded helical chains, whilst only a few examples with infinite single strand chains have been documented.[9]

In previous studies, we have used thioquinoline (SQ) substituted ligands with flexible linear spacers $CH_2(CH_2OCH_2)_nCH_2$ such as 1,5-bis(8-quinolylsulfanyl)-3-oxapentane (OESQ, $n = 1$)[10] and 1,8-bis(8-quinolylsulfanyl)-3,6-dioxaoctane (ODSQ, $n = 2$),[10] which contain sulfur, oxygen and nitrogen donors and obtained box-like tetranuclear complexes.[10] In those complexes, the thio-atoms seemed to have played important roles in the formation of discrete cage-molecules in which the folding effect of sulfur affords the backbone of the spacer to be perpendicular to the plane of the quinoline rings and to pucker up the ligand. It would be interesting to learn the effect of oxygen atoms at both ends of a long spacer chain as it should behave differently from sulfur. The ligand 1,3-bis(8-quinolyloxy)propane (PDOQ) with spacer $(CH_2)_3$ has been reported[5b] to be a reagent for lithium ion-selective transportation. Here we report a series of Ag(I) complexes containing the new highly flexible ligand *O*,*O*′-bis(8-quinolyl)-1,8-dioxaoctane (ODOQ) in which the spacer $(CH_2)_6$ bridges two oxaquinolyl rings (OQ).

Experimental

General comments

1,6-Dibromohexane was synthesized according to reported procedures.[11] n-Butyllithium was freshly prepared and titrated using the literature method[12] prior to use. Solvents THF and Et_2O were dried over sodium benzophenone and distilled before use. All other chemicals were of reagent grade from commercial sources and used without further purification. The C, H, N analyses were performed on a Perkin-Elmer 240 elemental analyser. IR spectra were recorded on a Nicolet 5DX FT-IR spectrophotometer in KBr discs in the 4000–400 cm^{-1} region, ^1H NMR spectra on an INOVA 500NB spectrometer with $SiMe_4$ as internal standard in DMSO-d_6.

CAUTION: although we have not had trouble with the silver perchlorate used, it should be handled with appropriate precautions, as perchlorate salts are known for their potential hazards.

Synthesis

***O*,*O*′-Bis(8-quinolyl)-1,8-dioxaoctane (ODOQ).** Standard Schlenk type apparatus was employed in this synthesis. n-Butyllithium (8.8 mmol, 1.2 M solution in Et_2O) was added slowly with stirring to a solution of 8-hydroxyquinoline (1.28 g,

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8.8 mmol) in 20 ml of THF at 0 °C, over a period of 30 min. A solution of 1,6-dibromohexane (1.07 g, 4.4 mmol) in THF (20 ml) was then added slowly over 1 h with stirring also at 0 °C. After stirring for a further 3 h, 10 ml of H_2O was added dropwise to quench the reaction. The volume of the solution was reduced to half and 30 ml of H_2O was added to the residue to precipitate the product. The pale yellow powder obtained was recrystallized from acetone, mp 102–103 °C, yield 78%. Found: C, 77.4; H, 7.35; N, 7.51. Calc. for $C_{24}H_{24}N_2O_2$: C, 77.4; H, 6.45; N, 7.53%. IR (cm^{-1}, KBr): 3054w, 3003w, 2947m, 2922m, 2868m, 1613w, 1568s, 1499s, 1464s, 1425m, 1374s, 1316s, 1261s, 1183m, 1104s, 1081m, 987m, 824m, 780m, 756m, 727m, 643w, 580w, 518w, 463w.

Preparation of silver(I) complexes. All complexes were prepared by a similar procedure. A solution of the silver salt AgX (0.12 mmol, X = ClO_4^- **1**, BF_4^- **2**, $CF_3SO_3^-$ **3**, or $CF_3CO_2^-$ **4**) in acetonitrile (10 ml) was added dropwise to a stirred solution of ODOQ (0.045 g, 0.12 mmol) in MeOH (10 ml) at room temperature then the mixture was stirred for 0.5 h. Pale yellow single crystals of **1**–**4** suitable for X-ray diffraction analyses were obtained by the slow diffusion of Et_2O into the clear reaction filtrate.

$[Ag(ODOQ)]_n(ClO_4)_n$ **1**: mp 178–179 °C. Yield 89%. Found: C, 50.0; H, 4.22; N, 4.82. Calc. for $C_{24}H_{24}AgN_2ClO_6$: C, 49.7; H, 4.14; N, 4.83%. IR (cm^{-1}, KBr): 3069w, 2934m, 2858w, 1614w, 1575w, 1506m, 1466m, 1377m, 1317m, 1264m, 1185w, 1108s, 1080s, 981m, 827m, 770m, 740w, 621m, 460w.

$[Ag(ODOQ)]_n(BF_4)_n$ **2**: mp 175–176 °C. Yield 85%. Found: C, 50.7; H, 4.36; N, 4.86. Calc. for $C_{24}H_{24}AgN_2BF_4O_2$: C, 50.8; H, 4.23; N, 4.94%. IR (cm^{-1}, KBr): 3116w, 3071w, 2934m, 2857w, 1615w, 1576m, 1506s, 1466s, 1427w, 1377m, 1371s, 1264s, 1186m, 1109s, 1078s, 1030s, 982m, 829s, 771m, 740m, 635w, 519w, 467w.

$[Ag(ODOQ)]_n(CF_3SO_3)_n$ **3**: mp 188–189 °C. Yield 83%. Found: C, 47.4; H, 3.85; N, 4.34. Calc. for $C_{25}H_{24}AgN_2SF_3O_5$: C, 47.7; H, 3.81; N, 4.45%. IR (cm^{-1}, KBr): 3128w, 2931w, 2839w, 1644m, 1572w, 1504m, 1482m, 1430m, 1368m, 1362s, 1257s, 1166s, 1089w, 1032s, 978m, 825m, 775m, 738m, 638w, 519w, 463w.

$[Ag(ODOQ)(CF_3CO_2)]_n$ **4**: mp 182–183 °C. Yield 82%. Found: C, 52.3; H, 4.18; N, 4.58. Calc. for $C_{26}H_{24}AgN_2F_3O_4$: C, 52.6; H, 4.05; N, 4.72%. IR (cm^{-1}, KBr): 3094w, 3053w, 2946m, 2869w, 1681s, 1616m, 1570m, 1502s, 1465s, 1428m, 1377s, 1318s, 1262s, 1206s, 1183, 1135s, 1105s, 986m, 930w, 825m, 780m, 756m, 724m, 639w, 586w, 517w, 467w.

Crystallography

Single crystals of **1**–**4** of suitable dimensions were mounted on glass fibres and data collections were performed on a Bruker SMART CCD diffractometer at 293 K by the ω scan technique using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The crystallographic data, data collection parameters and refinements are listed in Table 1. Data were corrected for Lorentz and polarization effects and absorption corrections were applied to all four complexes using the SADABS program.[13a] All the structures were solved by direct methods and refined by the full-matrix least squares method against F^2 using SHELXTL software.[13b]

The coordinates of the non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were included in the calculation isotropically but not refined. The fluorine atoms in anion $CF_3SO_3^-$ of **3** and C12 and C13 in **4** are disordered and each located at two positions with an occupancy of 0.5. The H-atoms for the ligand ODOQ were generated geometrically (C–H 0.96 Å).

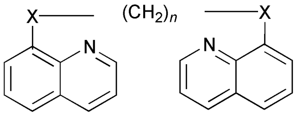
CCDC reference numbers 155605–155608.

See http://www.rsc.org/suppdata/dt/b1/b102525m/ for crystallographic data in CIF or other electronic format.

Results and discussion

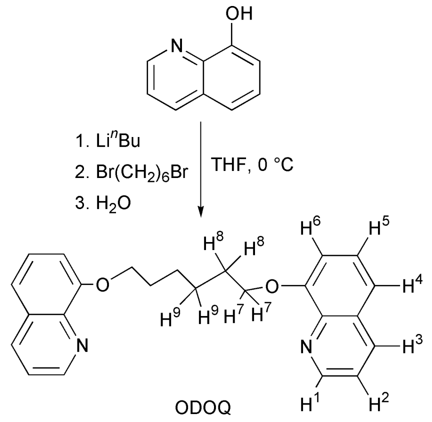
Synthesis

Compounds such as L^n containing flexible backbones $(CH_2)_n$ ($n \geq 2$) are soft ligands with rigid 8-oxaquinoline (X = O) or 8-thiaquinoline (X = S) as terminal groups. The mixed donor set N_2X_2 should enable them to behave as multidentate ligands with versatile coordination modes toward transition metal ions. For example, mononuclear complexes have been reported when n = 2–4.[14] As the spacer $(CH_2)_n$ elongates, the flexibility also increases and di- or poly-nuclear complexes can be constructed if careful selection of metal ions, counter anions, and solvents are applied.[15] These considerations prompted us to investigate the coordination behaviour of some of these (ligands with different n values) and the architecture of their complexes formed which various silver salts.



L^n(n = 2, 3, 4, 5, 6. X = S, O)

The ligand ODOQ was obtained by routine synthetic methods as shown in eqn. (1). The complexes **1**–**4** were synthesized by reaction of equimolar amounts of the ligand and the silver salt as depicted in eqn. (2).



(1)

$$n\text{ODOQ} + n\text{AgX} \rightarrow [\text{Ag(ODOQ)}]_n\text{X}_n \text{ or } [\text{Ag(ODOQ)(X)}]_n \quad (2)$$

X = ClO_4^-, **1** X = $CF_3CO_4^-$, **4**
X = BF_4^-, **2**
X = $CF_3SO_3^-$, **3**

In the reaction processes, products with Ag : ODOQ in 1 : 1 ratio were always obtained whether the molar ratio of the reactants was 1 : 1, 1 : 2, or 1 : 3, indicating that these complexes are the thermodynamically most stable species in these reaction media.

Crystal structures

Fragmental crystal structures of the helical complexes **1**, **3**, and **4** are depicted in Fig. 1–3, respectively, with selected atomic distances and bond angles listed in Table 2, in which are also listed some of the relevant structural parameters. The unit structure of the cation of **2** is similar to that of **3** and will not be shown. All complexes showed single stranded double helical structures in infinite chains, as exemplified by complex **1** in Fig. 4.

By taking the Ag(I) ions as two alternating but parallel backbones along the a-axis, the 1D polymer chain of these

Table 1 Crystallographic data for complexes **1**–**4**

	1	**2**	**3**	**4**
Formula	$C_{24}H_{24}AgClN_2O_6$	$C_{24}H_{24}AgBF_4N_2O_2$	$C_{25}H_{24}AgF_3N_2O_5S$	$C_{26}H_{24}AgF_3N_2O_4$
Formula weight	579.77	567.13	629.39	593.34
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic
Space group	*Pbca*	*Pbca*	*P*2(1)/*n*	*Pbca*
a/Å	18.505(4)	18.903(6)	13.271(3)	17.630(4)
b/Å	9.201(2)	9.094(3)	10.132(2)	8.991(2)
c/Å	27.389(6)	26.927(9)	19.264(5)	30.636(6)
a/°	90	90	90	90
β/°	90	90	91.562(4)	90
γ/°	90	90	90	90
V/Å^3	4663(2)	4629(3)	2589.4(11)	4856.2(18)
Z	8	8	4	8
μ/mm^{-1}	1.013	0.928	0.919	0.889
No. unique reflections	6717	6727	7307	5262
No. observed reflections [$I > 2\sigma(I)$]	3524	2214	4179	3361
R	0.0555	0.0741	0.0509	0.0362
wR	0.1456	0.2064	0.1286	0.0917

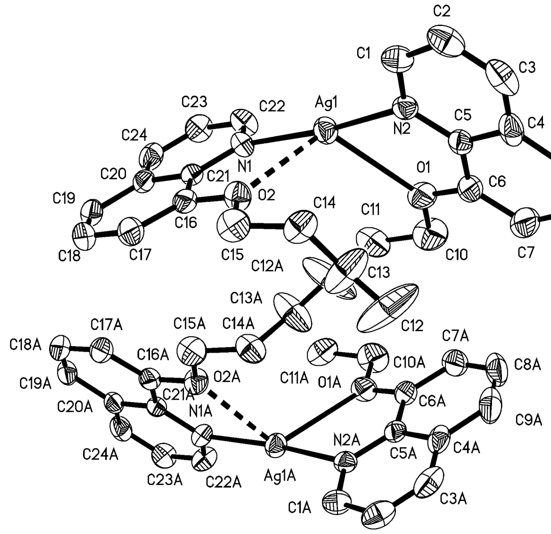


Fig. 1 Structure of the cation in complex $[Ag(ODOQ)]_n(ClO_4)_n$ **1** with ellipsoids drawn at the 30% probability level and the H-atoms omitted for clarity.

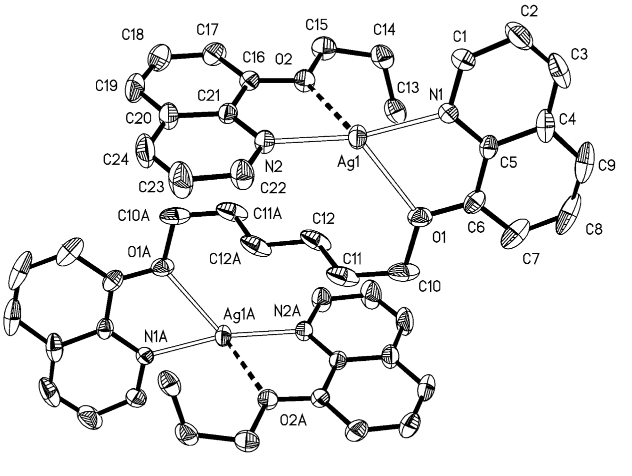


Fig. 2 Structure of the cation in complex $[Ag(ODOQ)]_n(CF_3SO_3)_n$ **3** with ellipsoids drawn at the 30% probability level and the H-atoms omitted for clarity.

complexes can be viewed as the ligands ODOQ wrapping around the Ag ions in a double-helical fashion in the form of an "∞", which is simultaneously in P and M forms as depicted in Fig. 5, thus forming a mesomeric single stranded complex. The Ag(I) ions in the complexes constitute the integral part of the

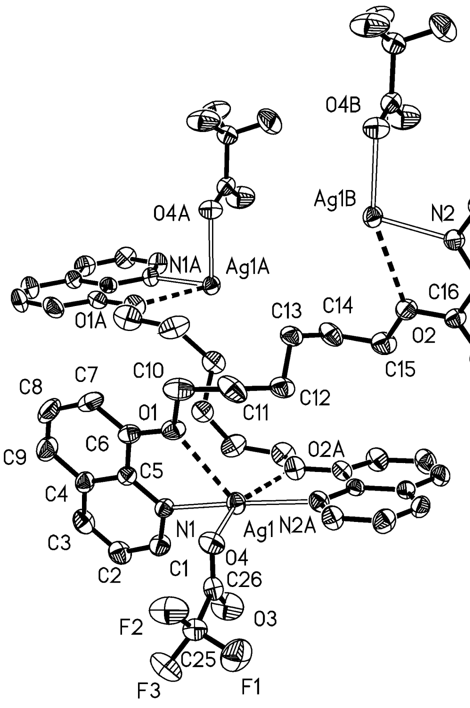


Fig. 3 Structure of complex $[Ag(ODOQ)(CF_3CO_2)]_n$ **4** with ellipsoids drawn at the 30% probability level and the H-atoms omitted for clarity.

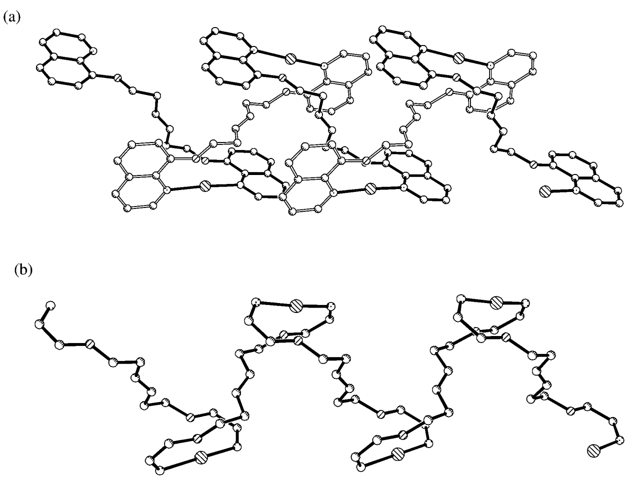


Fig. 4 Helical structure of complex **1**: (a) the helical chain of the molecule; (b) backbone atoms only.

Table 2 Selected atomic distances (Å) and bond angles (°) for complexes **1**–**4**[a]

1		**2**		**3**		**4**	
Ag1–N1	2.193(4)	Ag1–N1	2.179(6)	Ag1–N1	2.177(3)	Ag1–N1	2.240(2)
Ag1–N2	2.186(4)	Ag1–N2	2.193(6)	Ag1–N2	2.172(3)	Ag1–N2a	2.259(3)
Ag1–O1	2.613(4)	Ag1–O1	2.595(6)	Ag1–O1	2.595(3)	Ag1–O4	2.577(2)
Ag1 ··· O2	2.688(4)	Ag1 ··· O2	2.665(3)	Ag1 ··· O2	2.672(3)	Ag1 ··· O1	2.653(3)
						Ag1 ··· O2a	2.834(3)
N1–Ag1–N2	170.88(15)	N1–Ag1–N2	172.2(2)	N1–Ag1–N2	167.29(12)	N1–Ag1–N2a	162.19(9)
N2–Ag1–O1	67.5(3)	N1–Ag1–O1	67.8(2)	N1–Ag1–O1	67.71(11)	N2a–Ag1–O4	95.11(8)
N1–Ag1–O1	121.2(5)	N2–Ag1–O1	120.0(2)	N2–Ag1–O1	124.99(11)	N1–Ag1–O4	100.31(8)
C5–C6–O1	114.7(3)	C5–C6–O1	117.1(7)	C5–C6–O1	115.9(3)		
C6–O1–Ag1	111.8(3)	C6–O1–Ag1	111.3(5)	C6–O1–Ag1	111.9(2)		
Ag1–N2–C5	123.8(3)	Ag1–N1–C5	123.5(5)	Ag1–N1–C5	124.3(3)		
N2–C5–C6	121.2(5)	N1–C5–C6	119.1(7)	N1–C5–C6	120.1(4)		
$r_1 \cdots r_2$[b]	3.62		3.40		3.56		3.78
r_1/r_2[b]	1.8		1.9		0.6		1.6
r^a/r^b[c]	78.3		82.7		70.9		76.1

[a] Symmetry codes: for **4**, a $-x + 1/2, y - 1/2, z$. [b] $r_1 \cdots r_2$ and r_1/r_2 denote the centroid-to-centroid distance (Å) and dihedral angle (°) between the quinoline rings of two adjacent helical chains, respectively. [c] r^a/r^b Denotes the dihedral angle (°) between the quinoline rings around one silver(I) atom.

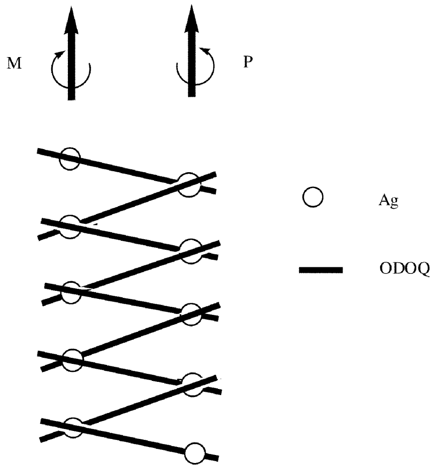


Fig. 5 Schematic view of the double-helical arrangement of complexes **1**–**4**.

backbones of the 1D polymer; each is coordinated by the N atoms of the oxaquinoline (OQ) subunits of two different ODOQ ligands in a linear fashion, continuation of such alternating ligations forms an infinitely extended mesomeric chain. The two OQ rings in one ligand are parallel to each other, while those of neighbouring ligands around a single silver ion are nearly perpendicular to each other, with dihedral angles in the range 70.9–82.7°. Chirality has been reported for complexes containing ligand strands ligated to Ag(I) with a single helical structure of identical absolute configuration (P).[16] However, the present complexes contain the Ag(I)-chelated ligands in single strand in double-helical arrangement (P + M) to accommodate the twisting chain of the long spacer $(CH_2)_6$ and to minimize the steric strain of the two terminal substituents. When the two parallel OQ moieties of one ligand which are oriented in opposite directions with respect to the spacer and link the two adjacent Ag ions, the ligand will be shaped like the symbol "~". Fig. 5 shows a schematic view of the single stranded double helical arrangement of the complexes with a helical pitch (Hp) of 8.991–10.132 Å.

Complex **1** contains the cation $[Ag(ODOQ)]_n^{n+}$ and anions ClO_4^- (Fig. 1). Strictly speaking, each Ag(I) ion is trigonally coordinated by two N atoms (N–Ag–N angle 170.88(15)°) of the OQ moieties from two independent ligands and an ethereal-oxo atom (Ag1–O1 2.613 Å). However, weak interaction of the second ethereal-oxo atom O2 with Ag (Ag1 ··· O2 2.688 Å) tetrahedrally distorts the coordination environment of Ag(I).

Complexes **2** and **3** (Fig. 2) have similar structures to that of **1**, except that the anions are different. Namely, the silver atoms in these complexes are 3-coordinated in trigonal geometry by N_2O atoms: two N from the OQ moieties of two different ligands and one ethereal-oxo atom (average Ag–N and Ag–O_{eth} of 2.175 Å and 2.595(3) Å in **2**, and 2.186 Å and 2.595(4) Å in **3**, respectively), while the remaining ethereal-oxo atom is only weakly interacting with Ag (Ag ··· O 2.665(3) Å in **2** and 2.672(3) Å in **3**).

Complex **4** with the strongly electronegative and ligating anion $CF_3CO_2^-$ provides quite a different coordination environment for the Ag(I) ions (Fig. 3), although still in trigonal geometry: the trigonal plane is composed of two N atoms from the OQ moieties of two individual ligands as usual, but now the third site is occupied by an oxygen donor from the anion $CF_3CO_2^-$ rather than from the ligand with an Ag–O4 distance of 2.577(2) Å. The two ethereal oxygen atoms are only weakly interacting with the silver ion with distances of 2.653(3) and 2.834(3) Å. As a result, the complex is neutral, with the shortest F ··· F contacts at a distance of 3.086 Å between neighbouring chains.

As we can see from the complexes **1**–**4**, the versatility of the coordination geometry of the Ag(I) ion is again displayed here. Considering the weak interactions of the ether oxygen atoms, trigonally arranged silver ions will become either tetra- or penta-coordinated in distorted tetrahedral or square pyramidal geometry.

When the OQ moiety is chelating to the silver ions as in **2** and **3**, rigidity of the chelate ring is shown by the constancy of the bite angles N–Ag–O and the chelate angles Ag–N–C and Ag–O–C: the former are acute with values near 68°, with the latter around 123° and 112°, respectively (with a difference of 10°), as observed in many complexes with 1,2-bidentate chelating ligands.[17]

The packing of these complexes in the crystal lattice is worth mentioning. The 1D infinite helical chains interact with each other *via* some weak intermolecular interactions[18] such as hydrogen bonding (C–H ··· O, C–H ··· F) and face-to-face π ··· π (in complexes **1**–**4**, Fig. 6a) and edge-to-face C–H ··· π (in complex **3**, Fig. 6b) stacking forming extended network structures. The centroid-to-centroid distances and dihedral angles between the quinoline rings of two adjacent helical chains are listed in Table 2, with the relative hydrogen bond distances and angles in Table 3. The counter anions in **1**–**3** are disposed between adjacent 1D cationic chains, while that in **4** is coordinated.

By comparison of these four complexes, it is observed that the cationic structures should be more controlled by the length of the spacer $(CH_2)_n$, *i.e.* the n values, than by the anions. Complex **4** exemplifies that even when the anion is coordinated to the Ag ion, the helicity of the complex chain is not greatly influenced. The present cases show that $n = 6$ in the spacer is a suitable value for mesomeric formation, in which both M and P helicities are present in one strand, compared to the Cu(I) complex of 2,6-bis[*N*-{2-(2-pyridyl)ethyl}formimidoyl]-1-methoxybenzene[5a] in which two individual helices are present in the unit cell, one of which is left handed (M) and the other right handed (P). Obviously, the resulting helical structure will be mainly determined by the flexiblity of ligands. Ligands with $n < 6$ or > 6 will be tempting candidates for complex formation, to find out the limit of the length of the spacers on the helicity of the complexes. Such work is now underway.

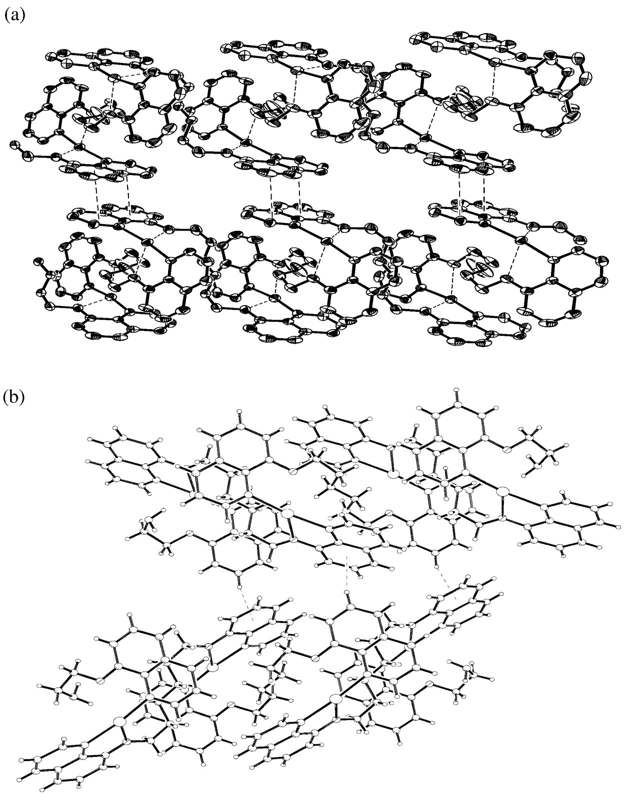


Fig. 6 Packing diagram: (a) with p–p stacking, as exemplified by complex **1**; (b) with edge-to-face C–H···π interactions in complex **3**.

Table 3 Hydrogen bond distances[a] (Å) and angles (°) for complexes **1**–**4**

Complex	Hydrogen bond	Distance	Angle
1	C24–H24···O3′	2.472	154.3
	C9–H9···O5′	2.514	143.8
2	C24–H24···F2′	2.527	149.8
	C2–H2···F3′	2.538	172.3
	C9–H9···F4′	2.443	140.1
3	C3–H3···O4′	2.390	153.8
	C1–H1···O5′	2.478	131.0
	C17–H17···O3′	2.485	145.0
	C24–H24···F2′	2.552	145.1
	C–H···π	3.076	
4	C10–H10···F2′	2.557	140.6

[a] Distances between the protons and oxygens (fluorines) or centroids of benzene rings. ′ Denotes the atoms from different helical chains in the crystal packing.

^{1}H NMR spectroscopy

The ^{1}H NMR spectral data of the ligand ODOQ and the complexes **1**–**4** are listed in Table 4, while the spectra in DMSO-d$_6$ for the ligand and **2** and **3** are shown in Fig. 7. Coupling constants ^3J and ^4J in the ranges 4–8.5 and 1–1.5 Hz, respectively, are observed for the compounds which conform to the normal values for *ortho*- and *meta*-protons, respectively, similar to those reported for OESQ or ODSQ ligated complexes.[10] In general, coordination of the ligand will induce downfield shift for the oxaquinolyl protons, but upfield shift for the hexyl protons. The coordination of quinoline-N atoms is illustrated by a slightly larger downfield shift of H^3 as compared to H^4, where the former is in the *para*-position of the N atom.

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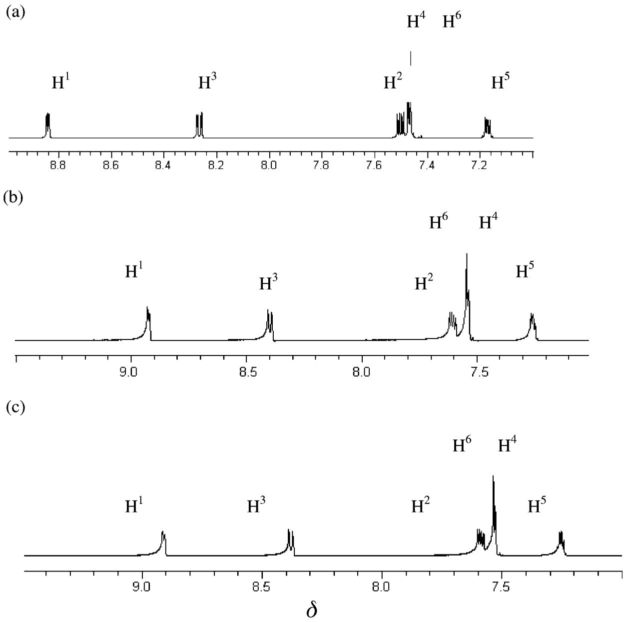

Fig. 7 Partial ^{1}H NMR spectra of the ligand ODOQ (a), complex **2** (b) and complex **3** (c) in DMSO-d$_6$.

Table 4 ^{1}H NMR spectroscopic data for ODOQ and complexes **1**–**4** in DMSO-d$_6$

	Chemical shift (ppm)									Coupling constant (Hz)						
Complexes	H^1	H^2	H^3	H^4	H^5	H^6	H^7	H^8	H^9	^3J(H^{1}H^2)	^4J(H^{1}H^3)	^3J(H^{2}H^3)	^3J(H^{4}H^5)	^3J(H^{5}H^6)	^4J(H^{5}H^7)	^3J(H^{7}H^8)
ODOQ	8.85	7.50	8.27	7.47[a]	7.19	7.46[a]	4.19	1.91	1.63	4	1.5	8.2	5.5	4	[b]	6.3
1	8.91	7.59	8.38	7.53[a]	7.25	7.53[a]	4.22	1.83	1.52	4	1.5	8.1	5	4	[b]	5.8
2	8.95	7.63	8.43	7.55[a]	7.27	7.56[a]	4.19	1.76	1.42	4	1.4	8.3	5.5	4	[b]	6.3
3	8.91	7.59	8.38	7.52[a]	7.25	7.53[a]	4.23	1.85	1.54	4	1.5	8.2	4.5	4.5	[b]	6.3
4	8.87	7.55	8.32	7.50[a]	7.22	7.51[a]	4.22	1.90	1.60	4	1.5	8	5	4.5	[b]	6.8

[a] Overlapped. [b] Not observed.

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