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Substituent-controlled assembly of helical complexes: synthesis, crystal and molecular structures of double helical silver(I) complexes with substituted quinquepyridines

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Both 6,6⁗-dimethyl-(dmqpy) and 6,6⁗-dimethyl-4′,4‴-diphenyl-2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine (dmpqpy) have been found to form dinuclear double helical silver(I) complexes $[Ag_2(dmqpy)_2][ClO_4]_2$ **1** and $[Ag_2(dmpqpy)_2][ClO_4]_2 \cdot 2H_2O$ **2**. The introduced terminal methyl groups play a crucial role in the assembly processes. According to their crystal structures, the ligand adopts the usual [2 + 3] co-ordination mode in **1** and the silver(I) is five-co-ordinated with a flattened and distorted trigonal-bipyramidal geometry. In **2** the ligand dmpqpy adopts a [2 + 1 + 2] mode and is unexpectedly tetradentate with the central pyridyl nitrogen atom having no direct co-ordination and acting as a rigid spacer. The silver(I) atoms are four-co-ordinated. It is supposed that the increased conjugation and rigidity caused by the phenyl groups at the 4′,4‴ positions makes it difficult for the central pyridine nitrogen to co-ordinate to Ag^I. Strong intramolecular π–π stacking interactions exist in complex **1**, but the stacking effects in **2** are much weaker. The NMR results indicate that both complexes adopt more symmetric configurations in solution than in the solid state.

Inorganic helical complex formation is a co-operative result of the ligand structure and the geometric co-ordination requirements of metallic ions. Several groups[1] have done much work to understand the coding principles which control this supramolecular chemistry. Oligopyridines[2] have aroused much interest for their ability to form helical complexes with first-row transition metals. It is usually concluded that substituents do not control the assembly of a helical complex, but are responsible for the detailed molecular geometry.[2-4] This is based on the facts that both 2,2′:6′,2″-terpyridine and 2,2′:6′,2″:6″,2‴-quaterpyridine and their substituted derivatives form double helicates with appropriate metals.[3,5-7] 2,2′:6′,2″:6″,2‴:6‴,2⁗-Quinquepyridine (qpy) can form both homo- and hetero-dinuclear double helicates,[8-10] but its 4,4‴-diphenyl derivative forms only a mononuclear complex with Co^{II},[11,12] although double helical complexes are formed with Cu^{II} and Ni^{II}.[12] There is no report of complexes formed by the 6,6⁗-disubstituted qpy derivatives.

In order to study the effects of 6,6⁗ substituents on the complex structure, we prepared the 6,6⁗-dimethyl (dmqpy) and 6,6⁗-dimethyl-4′,4‴-diphenyl (dmpqpy) derivatives.[13] Both formed double helical complexes with silver(I), while unsubstituted qpy produces only a mononuclear, near-planar five-co-ordinated complex under the same conditions.[14] The results indicate that substituents can control the assembly of double helical complexes. The crystal and molecular structures were determined.

Experimental

Syntheses

The compound dmqpy was prepared by the reaction of 2,6-bis(3-dimethylaminopropanoyl)pyridine dihydrochloride, 2-(6-methyl-2-pyridyl)-2-oxoethylpyridinium iodide and ammonium acetate in methanol (yield 84%), and dmpqpy was prepared by the reaction of 2,6-bis(1-pyridinioacetyl)pyridine diiodide, 1-(6-methyl-2-pyridyl)-3-phenylprop-2-en-1-one and ammonium acetate in glacial acetic acid according to the literature (yield 92%)[13] [Found: C, 77.85; H, 5.25; N, 16.55. Calc. for $C_{27}H_{21}N_6$ (dmqpy): C, 78.05; H, 5.10; N, 16.85. Found: C, 82.40; H, 5.15; N, 12.25. Calc. for $C_{39}H_{29}N_5$ (dmpqpy): C, 82.50; H, 5.15; N, 12.35%].

The compound dmqpy (or dmpqpy) (0.072 mmol) was suspended in a methanolic solution (20 cm^{-3}) of $AgNO_3$ (0.073 mmol). After refluxing for about 2 h, a clear yellow solution was obtained. Then 5 drops of saturated $LiClO_4$ solution in methanol were added. Cooling of the solution give pale yellow microcrystals. After filtration, the precipitate was recrystallized from acetonitrile solution by diethyl ether vapour diffusion (Found: C, 51.90; H, 3.50; N, 11.05. Calc. for $C_{27}H_{21}AgClN_5O_4$ **1**: C, 52.05; H, 3.40; N, 11.25. Found: C, 58.45; H, 4.05; N, 8.60. Calc. for $C_{39}H_{31}AgClN_5O_5$ **2**: C, 59.05; H, 3.95; N, 8.85%). FAB mass spectra: intense peaks around *m/z* 523, $[Ag(dmqpy)]^+$; 675, $[Ag(dmpqpy)]^+$.

Crystallography

Single crystals of complexes **1** and **2** suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether vapour into an acetonitrile solution of the complexes prepared as above.

Complex 1. Intensity data were collected on a Siemens R3m/V four-circle diffractometer with the variable ω-scan technique. An empirical absorption correction based on ψ-scan data was applied. All calculations were performed on a PC 486 computer with the SHELXTL PC program package.[15] The Patterson method yielded the positions of the metal and chlorine atoms, and all non-hydrogen atoms were derived from subsequent Fourier-difference syntheses. The hydrogen atoms of the ligands were placed in their calculated positions (C–H 0.96 Å), assigned fixed isotropic thermal parameters and allowed to ride on their respective parent atoms. Analytic expressions of atomic scattering factors were employed and anomalous dispersion corrections were incorporated. The refinement of the coordinates and anisotropic thermal parameters of the non-hydrogen atoms was carried out by full-matrix least-squares analysis on F^2; weighting scheme $w^{-1} = \sigma^2(F_o^2) + 0.045P^2 + 6.22P$, where $P = [\max.(F_o^2, 0) + 2F_c^2]/3$.

Complex 2. Data were collected on a Rigaku AFC7R diffractometer with graphite-monochromated Mo-Kα radiation using the ω–2θ scan technique to a maximum 2θ value of 45.0°. The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 2958 observed reflections $[I > 3.00\sigma(I)]$ and 462 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.045$, $R' = 0.062$; weighting scheme $w^{-1} = \sigma^2(F)$. All calculations were performed using the TEXSAN crystallographic package.[16] The crystal data, data collection and structure refinement for complexes **1** and **2** is summarized in Table 1, selected bond lengths and angles in Tables 2 and 3.

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.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/42.

Results and Discussion

Structure of $[Ag_2(dmqpy)_2][ClO_4]_2$ 1

Two enantiomers of the cation $[Ag_2(dmqpy)_2]^{2+}$ are identified in the lattice. The molecular structure of one is shown in Fig. 1 with the atom labelling scheme. A dinuclear formulation is confirmed and the substituted quinquepyridine ligands adopt a double helical configuration about the two equivalent silver atoms. It can be seen from Fig. 1(*a*) and Table 2 that the silver atoms are five-co-ordinated. The same co-ordination number has been reported for the $[Ag(qpy)]^+$ complex with near-planar geometry.[14] However, in complex **1**, the co-ordination geometry of silver can be regarded as a flattened distorted trigonal bipyramid. Atoms N(2), Ag(1), N(4a), N(5a) form the equatorial plane and the bond lengths Ag(1)–N(2) 2.330 Å, Ag(1)–N(4a) 2.346 Å and Ag(1)–N(5a) 2.381 Å are almost equal; N(1), N(3) form elongated bonds with Ag(1) (2.587 and 2.486) and occupy the two apical positions. In addition, N(1), N(2), N(3), Ag(1) form another plane which has a dihedral angle of 112° with the equatorial plane. Each of the two equivalent ligands is divided into two co-ordination segments in the usual fashion of [2 + 3], *i.e.* a bipyridine (bipy) segment and a terpyridine (terpy) segment and each metal is co-ordinated by the tridentate domain of one strand and the bidentate domain of the other to make a total co-ordination number of five. The helix is achieved by a series of twists of the ligand about the C–C bonds between adjacent pyridine rings. The dihedral angles between pyridine planes 1 and 2 (11.3), 2 and 3 (16.4), 3 and 4 (47.2) and 4 and 5 (6.9°) (the planes are numbered after the nitrogen atoms they contain; the angles of the other ligand strand have the same values) indicate that the major twists occur between rings 3 and 4 (or 3a and 4a in the other ligand), *i.e.* between the bipy and terpy segments. The twisting can be seen more clearly from the space-filling diagram in Fig. 1(*b*). As described by other authors, the deviation from coplanarity between individual pyridine rings resulting from the helical arrangement means a loss of conjugation among the aromatic rings, but the helical geometry results in two π–π stacking interaction systems between planar aromatic rings, one between terpy–terpy segments and the other between bipy–bipy segments from the different ligand molecules. Both stacking distances are in the range 3.38–3.42 Å, which means strong interaction.[2] In addition there is a weak intermolecular π–π stacking effect in the crystal lattice. The stacking distance is about 3.70 Å. This stacking occurs among different enantiomers which are in parallel alternately in the *z* direction to make an infinite chain.

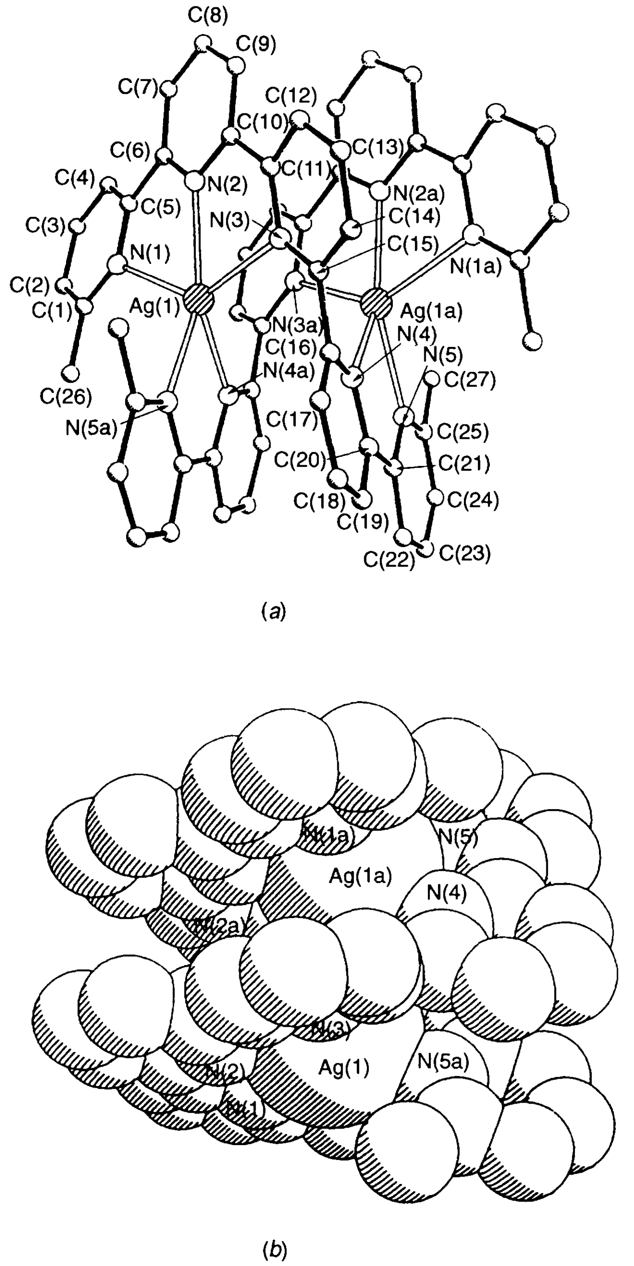

Fig. 1 Molecular structure of complex **1** with the atom labelling scheme (*a*) and a space-filling diagram (*b*)

The two-fold rotation axis in the *b* direction which bisects the molecule between the two silver atoms can generate the other half of the molecule which contains Ag(1a) and the other ligand strand. The helical radius is about $b/3 = 5.0$ Å and the pitch height is about $c/2 = 8.1$ Å. The Ag ··· Ag distance is 3.48 Å.

Compared with the mononuclear near-planar conformation in the unsubstituted qpy silver(I) complex,[14] the double helical conformation of dmqpy complex is caused by the two methyl groups introduced at the 6,6'''' positions which would result in large steric effects if a planar conformation were adopted in the dmqpy complex. So the assembly of the double helix is a substituent-controlled process. It has been proposed previously[1] that the cause of the formation of the double helical silver complex of a qpy analogue, 2,6-diacetylpyridine bis(6-chloro-2-pyridylhydrazone),[17] is that the introduction of the two chlorine atoms at the two terminal positions enlarges the hole size of the ligand, so that the silver atoms are not large enough to fit into the hole and form a five-co-ordinate planar structure with only one ligand. However it is perhaps more appropriate to say that it is the steric effect of the terminal groups that makes the ligand unable to adopt a planar configuration, the double helix formation being the inevitable result.

The ^{1}H NMR spectrum of complex **1** show eight proton environments in the aromatic chemical shift range δ 7–8 (Fig. 2) indicating a higher symmetry in solution than that in the solid state. This is in accord with a mononuclear monohelical form as was reported for the Co^{II}–qpy complex[11] or a relaxed double helical form of the complex which has D_2 symmetry and all four ligand halves equivalent. The solvent effect is responsible for the change of conformation in solution.

Structure of [Ag$_2$(dmpqpy)$_2$][ClO$_4$]$_2$·2H$_2$O 2

The molecular structure of the right-handed enantiomer is shown in Fig. 3 The bonds to the two terminal pyridyl nitrogen atoms are similar [Ag–N(2) 2.466(5), Ag–N(4) 2.465(5) Å] and longer than that to the two inner pyridyl nitrogen atoms [Ag–N(1)/Ag–N(3) 2.380(4) Å]. The Ag–N(5) and Ag–N(6) distances are 2.755 and 2.726 Å respectively, much longer than the other four. So, neither of these nitrogen atoms co-ordinates directly to Ag, but each has weak interactions with Ag and Ag′ simultaneously, as observed previously.[17] The silver atom should be regarded as four-co-ordinated.

As in complex **1**, the ligand dmpqpy in **2** adopts a double helical configuration about the two equivalent silver(I) atoms. However, each of the two ligands is divided into three segments in the unusual fashion [2 + 1 + 2] with the two terminal bipy moieties co-ordinating to the two silver atoms and the remaining central pyridine nitrogen atoms only weakly involved in the co-ordination. So, dmpqpy actually acts as a tetradentate ligand and the central pyridyl ring plays the role of a rigid spacer rather than of a donor. This is the first example of qpy derivatives adopting such a co-ordination mode although sharing of a pyridyl ring equally between two metals is known for complexes

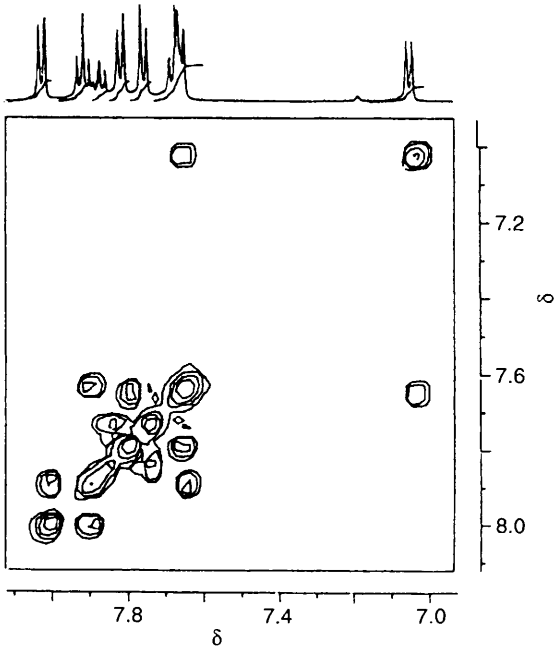

Fig. 2 Proton NMR spectrum of complex **1** in acetonitrile solution (CD$_3$CN, 500 MHz): δ 7.02 (2 H, d, H^{3,5}, H$^{5'''',3''''}$), 7.66 (2 H, t, H^4, H$^{4''''}$), 7.79 (2 H, d, H^{5,3}, H$^{3'''',5''''}$), 7.63 (2 H, d, H$^{5',3'}$, H$^{3''',5'''}$), 7.73 (2 H, d, H$^{3''}$, H$^{5''}$), 7.84 (1 H, t, H$^{4''}$), 7.89 (2 H, t, H$^{4'}$, H$^{4'''}$), 8.00 (2 H, d, H$^{3',5'}$, H$^{5''',3'''}$)

Table 1 Summary of crystal data, data collection and structure refinement for complexes **1** and **2**

Compound	[Ag$_2$(dmqpy)$_2$][ClO$_4$]$_2$ **1**	[Ag$_2$(dmpqpy)$_2$][ClO$_4$]$_2$·2H$_2$O **2**
Empirical formula	C$_{27}$H$_{21}$AgClN$_5$O$_4$	C$_{39}$H$_{31}$AgClN$_5$O$_5$
M	622.81	793.03
T/K	293(2)	293(1)
a/Å	20.479(2)	24.540(3)
b/Å	14.905(2)	14.633(2)
c/Å	16.233(7)	20.716(2)
β/°	96.97(2)	111.329(8)
U/Å^3	4918(2)	6929(1)
D_c/Mg m^{-3}	1.682	1.520
λ(Mo-Kα)/Å	0.710 73	0.710 69
μ(Mo-Kα)/cm^{-1}	9.74	7.10
F(000)	2512	3232
Crystal size/mm	0.2 × 0.26 × 0.32	0.20 × 0.20 × 0.30
No. reflections measured	3995	4445
No. unique reflections	3875	4313
Variables	339	462
Goodness of fit indicator	1.075 (on F^2)	1.65 (on F)
R_1	0.0430	0.042
wR_2	0.1068	0.057

Common details: monoclinic, space group $C2/c$, Z 8.

Table 2 Selected bond lengths (Å) and angles (°) for complex **1**

Ag(1)–N(2)	2.330(4)	Ag(1)–N(4a)	2.346(4)
Ag(1)–N(5a)	2.381(4)	Ag(1)–N(3)	2.486(4)
Ag(1)–N(1)	2.587(4)		
N(2)–Ag(1)–N(4a)	139.92(12)	N(2)–Ag(1)–N(5)	148.93(13)
N(4a)–Ag(1)–N(5a)	70.70(13)	N(2)–Ag(1)–N(3)	69.68(12)
N(4a)–Ag(1)–N(3)	123.41(12)	N(5a)–Ag(1)–N(3)	99.39(12)
N(2)–Ag(1)–N(1)	67.74(12)	N(4a)–Ag(1)–N(1)	91.54(12)
N(5a)–Ag(1)–N(1)	116.18(12)	N(3)–Ag(1)–N(1)	137.37(12)

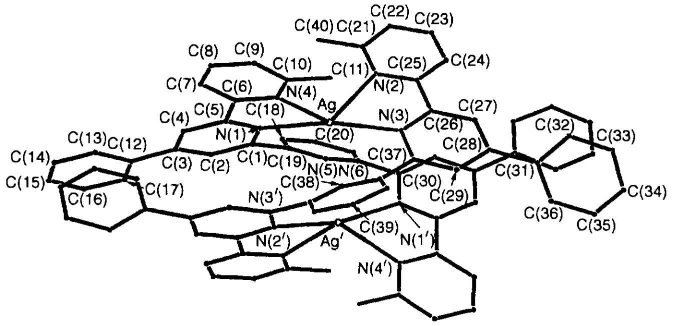

Fig. 3 Molecular structure of complex **2** with the atom numbering scheme

Table 3 Selected bond lengths (Å) and angles (°) for complex **2**

Ag–N(1)	2.380(4)	Ag–N(2)	2.466(5)
Ag–N(3)	2.380(4)	Ag–N(4)	2.465(5)
N(1)–Ag–N(2)	116.2(2)	N(1)–Ag–N(3)	168.5(2)
N(1)–Ag–N(4)	68.7(2)	N(2)–Ag–N(3)	68.6(2)
N(2)–Ag–N(4)	122.0(2)	N(3)–Ag–N(4)	118.6(2)

of Cu^I and Ag^I of terpy-based ligands.[3,18] The helix is achieved by a series of twists between the adjacent pyridine rings about the interannular C–C bond. The dihedral angles of between rings 4 and 1 (12.5), 1 and 6 (36.8), 6 and 1′ (36.8), 1′ and 4′ (12.5), and 2 and 3 (2.7), 3 and 5 (36.1), 5 and 3′ (36.1) and 3′ and 2′ (2.7°) (pyridine planes numbered after the nitrogen atoms they contain) in the two ligand strands show that two equal major twists occur between the 2,2′-bipyridyls and the central 2,6-pyridyl rings in each strand. A C_2 rotation axis exists in the molecular structure, which lies in the *y* direction of the crystal and bisects the molecule between the two silver atoms, passing through atoms C(20), C(39), N(5), N(6). This operation generates not the other ligand strand but the other half of the same ligand. So the ligand itself has C_2 symmetry and only one of the two bipyridyls in a ligand is unique. However, the two ligands are not equivalent crystallographically as indicated by the different twist angles. Atoms C(20), N(5), Ag, Ag′, N(6) and C(39) are coplanar and form a rhomb. The co-ordination geometry at Ag(I) can be regarded as a distorted tetrahedron. Atoms N(1), N(3), N(4), Ag are approximately coplanar. The silver–silver distance in complex **2** is 3.22 Å, significantly longer than that in silver metal (2.899 Å), but shorter than that in **1**. This shorter distance is in accord with the smaller major twisting angle of 36.1° (or 38.8° in the other strand) in **2** than that of 47.2° in **1**, but it is not short enough to result in direct metal–metal interaction. The pitch height is about $a/2 = 12.3$ Å. The helical radius is about $b/3 = 5.0$ Å in the *y* direction [half the distance from C(20) to C(39)] and the most external diameter is about $c/2 = 10.3$ Å in the *z* direction. The phenyl groups have adopted different relative positions compared to that in the mononuclear complex formed by 4′,4‴-diphenyl derivative of qpy.[11] In the latter case, the dihedral angles between the phenyl rings and the attached pyridyl rings are 26.4 and 18.8°, but in complex **2** the two dihedral angles in one ligand strand have the same value of ≈0°, *i.e.* the phenyl rings are coplanar with the attached pyridyl rings, but the corresponding two in the other strand have the same value of 24.4°. A weak π–π stacking effect is observed in **2** with a stacking distance of 3.8–3.9 Å between rings 1 and 3′ and 1′ and 3. However, as indicated above, the related phenyl rings from different ligand molecules are not parallel to each other and do not take part in the stacking interaction. The formation of the double helical conformation also results from the two methyl groups introduced into the 6,6⁗ positions as explained above for complex **1**.

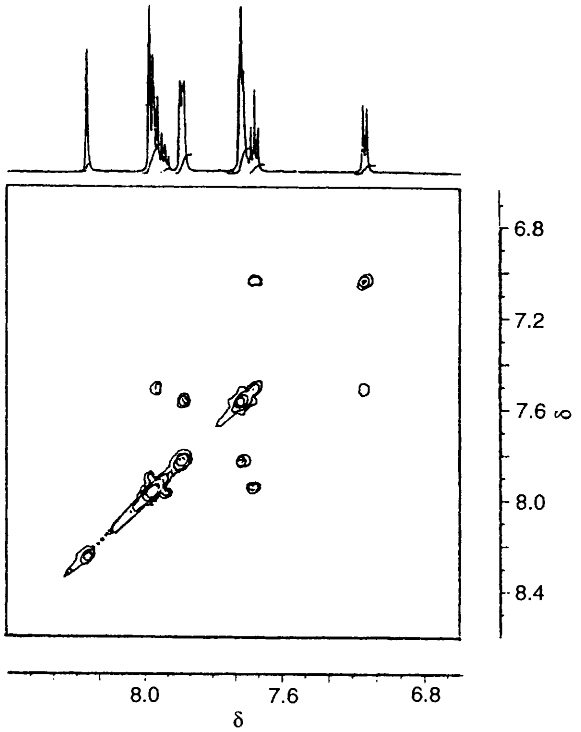

Fig. 4 Proton NMR spectrum of complex **2** in acetonitrile solution (CD_3CN, 500 MHz): δ 7.03 (2 H, d, $H^{3,5}$, $H^{5'''',3''''}$), 7.50 (2 H, t, H^4, $H^{4''''}$), 7.90 (2 H, d, $H^{5,3}$, $H^{3'''',5''''}$), 7.56 (2 H, s, $H^{5',3'}$, $H^{3''',5'''}$), 8.24 (2 H, s, $H^{3',5'}$, $H^{5''',3'''}$), 7.95 (2 H, d, $H^{3''}$, $H^{5''}$), 7.89 (1 H, t, $H^{4''}$)

No intermolecular stacking interactions are observed in complex **2**, but one unique water molecule [O(5)] is located in the crystal lattice. The contact distances O(5) ··· O(4) (3.17 Å) and O(5) ··· O(3) (3.43 Å) indicate hydrogen-bond formation between water molecules and perchlorate counter ions.

We could not completely resolve the ^{1}H NMR spectrum of complex **2** (Fig. 4), but from the two-dimensional correlation spectrum the protons on the pyridyl rings were assigned. The results reveal a highly symmetric conformation of dmpqpy in the complex in solution. A sequence change can be observed between the resonances of $H^{4''}$ and $H^{3''}$, $H^{5''}$ compared to that for complex **1** as a result of the weaker interaction of the central pyridyl nitrogen atom in dmpqpy with silver. Although we were unable to obtain a two-dimensional C–H correlation NMR spectrum owing to the limited solubility in known deuterium-labelled solvents, the ^{13}C NMR spectrum recorded shows 18 carbon environments, in accord with only one half of the ligand being unique. So, a more symmetric structure is expected for complex **2** in solution than that in the crystal state.

The difference between complexes **1** and **2** is apparent. This is certainly caused by the two 4′,4‴ phenyl groups introduced in dmpqpy. The different behaviours of the two ligands when co-ordinated to silver(I) are caused by steric effects and the increased conjugation in dmpqpy which makes it more rigid and difficult to adopt an adequate conformation for the central pyridyl nitrogen to co-ordinate to such a large metal ion as silver(I). In addition, the electron-withdrawing effect of the two phenyl groups disfavours coordination. However, in the mixed-valence complex formed by dmpqpy and copper(I,II)[19] the principal features are similar to that in the corresponding complex of unsubstituted quinquepyridine although the two phenyl groups enlarge the external diameter of the double helix. The apparent difference is perhaps caused by the smaller ionic radius of copper(I).

Conclusion

Although only a mononuclear complex can be formed between unsubstituted qpy and Ag^I,[14] the introduction of substituents into the 6,6‴ positions results in the formation of double helical complexes for both of the ligands described here. The reason is the greater steric effects caused by the introduced terminal groups if an all-*cis* coplanar configuration is adopted than are caused by the terminal hydrogen atoms in unsubstituted qpy. So it can be deduced that substituents can play an essential role in determining whether a double helicate can form for a certain donor set as that in qpy. From the present results and the literature, it can be deduced that to construct a double helical complex four factors must be considered: (1) the ligand donor set (an adequate distribution of the donor atoms is indispensable); (2) the co-ordination geometry of the metal ion; (3) substituent effects (the presence of substituents at crucial positions can also control the assembly process); (4) the metal-ion radius.

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