Charge Alone is Not Sufficient to Cause Helication with 2,2' : 6',6" : 6",2''' : 6''',2''''-Quinquepyridine; Crystal and Molecular Structure of 2,2' : 6',6" : 6",2''' : 6''',2''''-Quinquepyridinium Bishexafluorophosphate

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2,2' : 6',2" : 6",2''' : 6''',2''''-Quinquepyridine (qpy) forms a shallow monohelical (1 : 1) complex with silver(I), but double-helical (2 : 2) complexes with first-row transition-metal ions, and the crystal structure of [H₂qpy][PF₆]₂ reveals that the cation is near-planar rather than helical, and adopts a cis,trans,trans,cis conformation about the interannular C–C bonds [$P2_1/a$, $a = 12.489(4)$, $b = 17.308(7)$, $c = 12.597(3)$ Å, $\beta = 93.92(2)°$]; the features leading to a helication are discussed.

The control of molecular and supramolecular interactions in chemical and biological arrays is an area of intense interest.[1,2] We and others have recently utilised the stereochemical requirements of transition-metal ions to control the assembly of topologically novel ligand arrays, of which double-helical, triple-helical, catenated and knotted systems are specific examples.[3–8] We have been probing the detailed features which lead to helication with 2,2' : 6',2" : 6",2''' : 6''',2''''-quinquepyridine (qpy)[9–16] and other oligopyridines.[17–21] This communication describes attempts to distinguish between steric and charge control of helication with this ligand.

Linear oligopyridines are planar in the solid state, with a *transoid* arrangement of pyridine rings about each interannular C–C bond (Fig. 1, 1a)[21–27] In order to chelate to a metal ion, it is necessary to adopt an approximately coplanar *cisoid* conformation 1b about the interannular C–C bond. We have previously shown that in the planar all *cisoid* conformation 1c
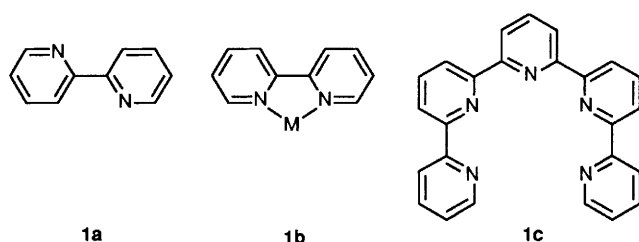
qpy possesses a bonding cavity of radius 2.5 Å, which corresponds to a hole size of 1.1 Å.[11]

Upon interaction with silver(I) ($r \approx 1.0$ Å) which has no orbitally dictated stereochemical preference, qpy forms an approximately planar (actually shallowly helical) five-coordinate complex cation [Ag(qpy)]⁺. In contrast, interaction with metal ions which are significantly smaller than the cavity results in the formation of the complex [M₂(qpy)₂Xₙ]ⁿ⁺. These species are double helical and arise from twisting of the ligand about interannular C–C bonds to present 2,2'-bipyridyl and 2,2' : 6',2"-terpyridyl sections to different metals (Fig. 2). We have now probed the balance between steric and electronic control of this process by investigating the role of the proton, which may be regarded as a metal ion which is too small to fill the cavity but which has no specific stereochemical requirements.
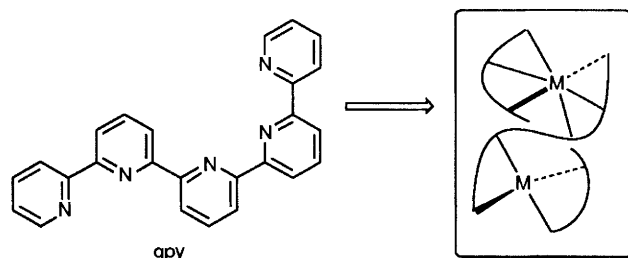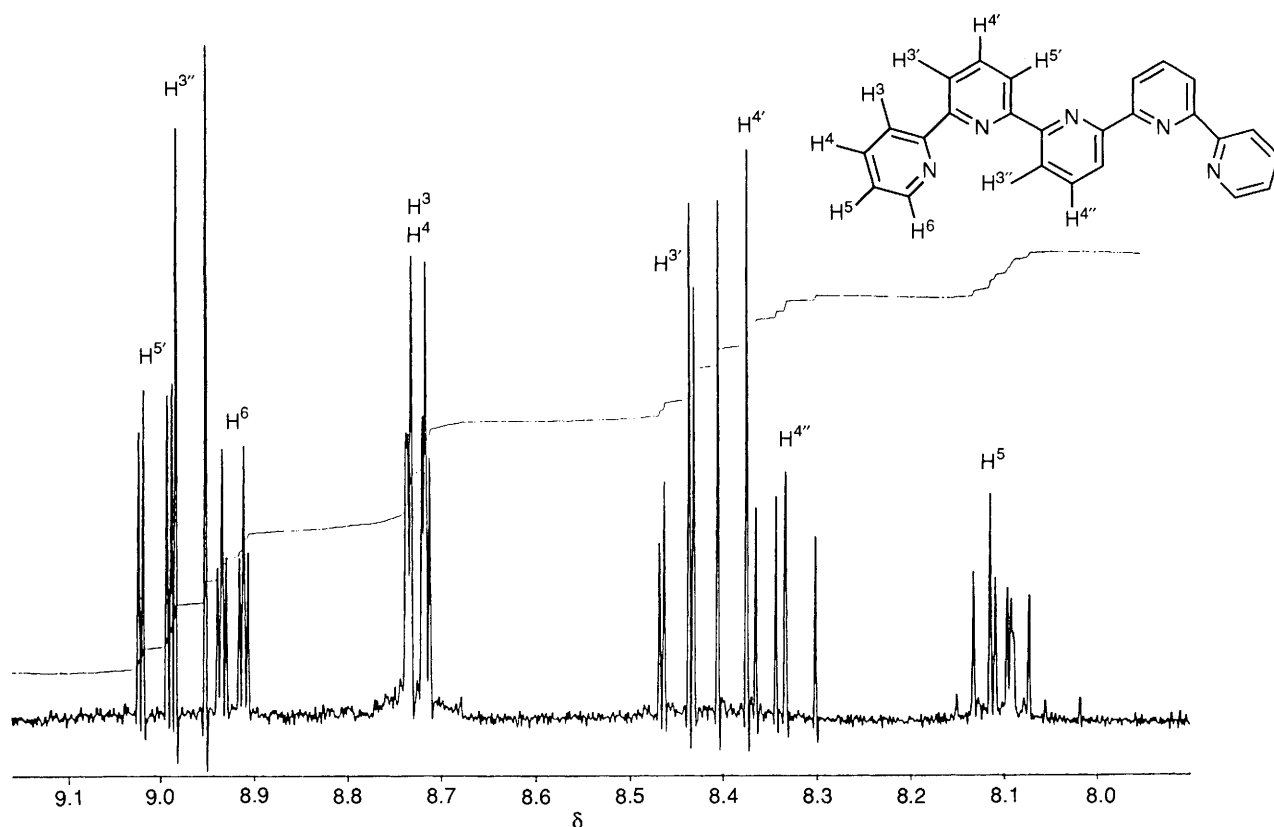

1a   1b   1c

Fig. 1

qpy

Fig. 2

Fig. 3 250 MHz ^{1}H NMR spectrum of a solution of [H$_2$qpy][PF$_6$]$_2$ in CD$_3$CN

The relatively insoluble compound qpy dissolves in warm methanolic HCl to give a clear colourless solution containing [H$_2$qpy]$^{2+}$, from which the salt [H$_2$qpy][PF$_6$]$_2$ is precipitated upon the addition of [NH$_4$][PF$_6$]. The fast atom bombardment (FAB) mass spectrum of the salt exhibits a single ion at m/z 388 ({Hqpy}$^+$). The ^{1}H NMR spectrum of a solution of the salt (Fig. 3) exhibits a high degree of symmetry on the NMR timescale and an equivalence about the central pyridine ring. All resonances are shifted with respect to the parent ligand. Recrystallisation from methanol yielded very poor quality crystals, but we eventually obtained one of X-ray standard and we have determined the crystal and molecular structure of the salt in order to further probe the conformation.†

The crystal structure of a formula unit of [H$_2$qpy][PF$_6$]$_2$ is shown in Fig. 4. The cation is near-planar and exhibits a *cis,trans,trans,cis* conformation about sequential interannular C–C bonds. Although approximately planar, there are slight deviations from planarity (angles between mean planes, 1–2, 6.4°; 2–3, 2.7°; 3–4, 5.2°; 4–5, 4.7°, rings numbered after the nitrogen atoms they contain). The *cis* conformations are associated with the rings which are coordinated to the acidic proton; although this proton was not directly located, it was placed by analogy with other 2,2'-bipyridinium salts which have been structurally characterised, and on the basis of short contacts with the hexafluorophosphate anions [F(7)–N(5), 2.902; F(7)–N(4), 3.742; F(2)–N(1), 2.840; F(2)–N(2), 3.721
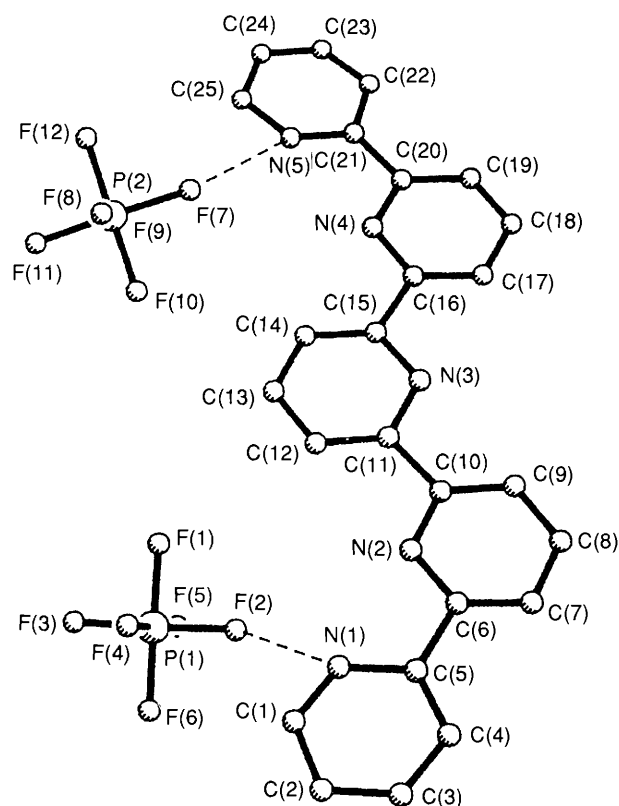
Fig. 4 Crystal and molecular structure of a formula unit of [H$_2$qpy][PF$_6$]$_2$ showing the numbering scheme adopted

Å] which are hydrogen bonded to the 'acidic' proton. This is also reflected in the bending of the terminal pyridine rings towards this proton, resulting in the reduction of the angles
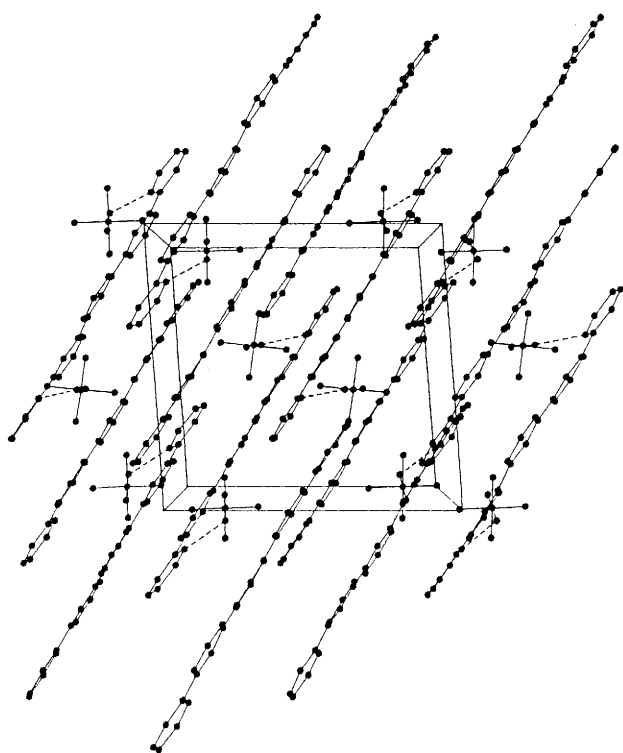
Fig. 5

between rings 1–2 and 4–5 [$\angle$N(1)–C(5)–C(6), 115.9(11); $\angle$N(2)–C(6)–C(5), 113.0(11)°] compared to those with the central ring [$\angle$C(9)–C(10)–C(11), 123.3(11); $\angle$N(3)–C(11)–C(10), 114.4(10)]. The rings which are not 'linked' by protonation (2–3–4) exhibit the expected *trans,trans* conformation. The cations [H_2qpy]$^{2+}$ form coplanar stacks within the crystal lattice along the *b* axis (Fig. 5), with the interplanar contacts lying within the range 3.51–3.69 Å. Pairs of coplanar cations are displaced along the *a* axis, such that the closest contacts are between rings 2 and 1′,3 and 2′,4 and 3′, and 5 and 4′. It is significant to note that the coordination of the ligand to the proton results in a closing up of the interplanar contacts to distances typical of π-stacking interactions, and in very marked contrast to the longer distances (>6 Å) observed in the related free ligand oligopyridines 2,2′ : 6′,2″ : 6″,2‴-quaterpyridine,[21] 4′-phenyl-2,2′ : 6′,2″-terpyridine[22] and 6,6″=dibromo-4′-phenyl-2,2′ : 6′,2″-terpyridine.[23]

We have also performed extensive molecular-mechanics calculations upon qpy and the various possible protonated forms.[27] Monoprotonation of qpy to [Hqpy]$^+$ could lead to a range of structures; the global minimum is that in which the proton is found within the cavity of a *cis,cis,cis,cis* ligand interacting with all five nitrogens. Significantly, only small interannular twistings are observed in this case, resulting in a shallow helical conformation reminiscent of the structure we have already observed for the complex [Ag(qpy)]$^+$. Diprotonation leads to a global minimum with a *cis,trans,cis,cis* conformation. One proton is associated with *two* rings whereas the second is associated with *three* rings; the *trans* junction is observed between the 'bipy' and 'terpy' parts. This minimum is considerably stabilised with respect to the *cis,trans,trans,cis* conformation which we observe in the crystal structure of [H_2qpy][PF_6]$_2$. We suggest that this may be attributed to hydrogen bonding with the hexafluorophosphate anions together with any contribution from intermolecular charge-transfer π-type interactions. It is significant that the molecular mechanics suggests that the 'terpy' portion interacts

very asymmetrically with the proton, giving two short and one long contact; the long contact is to ring 3.

We consider that we are now in a position to further delineate the conditions required for the helication of qpy ligands. Firstly, it is necessary to interact with a charged species. This allows intermolecular charge-transfer interactions, although the overall importance of these in determining the structures remains to be determined. Secondly, the charge centre has to be 'too small' for the bonding cavity of the qpy ligand in all *cis* conformation. Thirdly, it is necessary for the charge centre to impose some degree of spatial constraint upon the distribution of nitrogen donors. This spatial constraint may be ligand-field in origin or size dominated (*i.e.* a proton is too small to fit five pyridine ligands about it at reasonable distances).

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