Mono- and Di-nuclear Helical Complexes of 2,2′:6′,2″:6″,2‴:6‴,2⁗-Quinquepyridine (qpy) and its 4′,4‴-Disubstituted Derivatives; Crystal and Molecular Structures of [Co(bcpqpy)(H_2O)(MeOH)][PF_6]$_2$ and [Ni_2(bmtqpy)$_2$(O_2CMe)][PF_6]$_3$ [bcpqpy and bmtqpy = bis(*p*-chlorophenyl) and bis(methylthio) derivatives]†

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A series of substituted 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine ligands has been prepared and its co-ordination chemistry investigated. The presence of substituents on the ligand does not alter the co-ordination chemistry, and double-helical complexes of 2:2 metal:ligand stoichiometry are obtained with nickel(II) and copper. Cobalt(II) can form either 1:1 or 2:2 solid-state species, but in solution only mononuclear seven-co-ordinate complex ions are present. The crystal and molecular structures have been determined for the mononuclear complex [Co(bcpqpy)(H_2O)(MeOH)][PF_6]$_2$ [bcpqpy = 4′,4‴-bis(*p*-chlorophenyl)-2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine] [monoclinic, space group $P2_1/a$, a = 17.441(4), b = 11.765(4), c = 20.402(6) Å, β = 105.24(2)°, Z = 4, R = 0.085, R' = 0.0766] and the double-helical complex [Ni_2(bmtqpy)(O_2CMe)][PF_6]$_3$ [bmtqpy = 4′,4‴-bis(methylthio)-2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine] [orthorhombic, space group *Pnna*, a = 16.916(17), b = 25.661(25), c = 16.054(14) Å, Z = 4, R = 0.086, R' = 0.088].

There has been considerable recent interest in the stereochemical consequences of metal–ligand interactions and the utilisation of such interactions in the design of topologically novel molecular systems.[1] In particular, ligands incorporating oligopyridine metal-binding domains have proved to be versatile, allowing the preparation of helical, interlinked and knotted molecular arrays.[2] We have demonstrated that the co-ordination compounds formed by the higher oligopyridines provide a facile entry into double-helical systems,[3] and report in this paper some observations regarding the ready interconversion of single- and double-helical complexes with certain metal ions, and a systematic study of the effects of ligand substitution upon the formation of helical complexes. Some of these results have been reported in an earlier communication.[4]

Experimental

Infrared (IR) spectra were recorded on a Philips PU9624 Fourier-transform spectrophotometer, with the samples in compressed KBr discs, proton NMR spectra on a Brüker WM-250 spectrometer. Fast atom bombardment (FAB) and electron-impact (EI) mass spectra were recorded on a Kratos MS-50 spectrometer with 3-nitrobenzyl alcohol as the matrix for the FAB spectra. Electron spin resonance (ESR) spectra were recorded on a Varian E-109 spectrometer as frozen acetonitrile glasses at 90 K. Electrochemical measurements were performed using an AMEL model 553 potentiostat, model 567 function generator and model 721 integrator connected to an X–Y recorder *via* an AMEL model 560/A interface. A conventional three-electrode configuration was used, with platinum-bead working and auxiliary electrodes and Ag–AgCl or Ag–Ag$^+$ electrodes as references. The solvent was purified acetonitrile in all cases, and the base electrolyte was 0.1 mol dm^{-3} [NBu_4][BF_4], recrystallised twice from ethanol–water. Ferrocene was added at the end of each experiment as an internal standard.

2,2′:6′,2″:6″,2‴:6‴,2⁗-Quinquepyridine (qpy),[5] its 4′,4‴-diphenyl (dpqpy)[5,6] and 4′,4‴-bis(methylthio) (bmtqpy)[7] derivatives and *N*-[1-oxo-2-(2-pyridyl)ethyl]pyridinium iodide[5] were prepared by literature methods.

Preparations.—2,6-*Bis*[1-*oxo*-3-(p-*tolyl*)*prop*-2-*enyl*]*pyridine*. 2,6-Diacetylpyridine (2.5 g, 0.015 mol), 4-methylbenzaldehyde (7.5 cm^3, 0.074 mol) and diethylamine (10 cm^3) were heated to reflux in propan-1-ol (60 cm^3) for 12 h and then allowed to cool. The yellow crystalline precipitate was filtered off and washed with ice-cold methanol (3.5 g, 64%). IR: 1670s, 1602s, 1568m, 1511m, 1412w, 1331s, 1244w, 1208w, 1031s, 987s, 802s, 737w, 692w, 662m and 495m cm^{-1}. *m*/*z* 366 (positive-ion FAB). Details of all ^{1}H NMR spectroscopic results for bis(enone) compounds and ligands are contained in Table 1.

4′,4‴-*Bis*(4-*tolyl*)-2,2′:6′,2″:6″,2‴:6‴,2⁗-*quinquepyridine* (btqpy). 2,6-bis[1-oxo-3-(*p*-tolyl)prop-2-enyl]pyridine (0.367 g, 1 mmol), *N*-[1-oxo-2-(2-pyridyl)ethyl]pyridinium iodide (0.652 g, 2 mmol) and ammonium acetate (4 g) were heated to reflux in a mixture of ethanol (10 cm^3) and glacial acetic acid (1 cm^3) for 3 h and then cooled. The creamy white product was filtered off and recrystallised from toluene to yield btqpy as an off-white solid (0.465 g, 82%). IR: 1605m, 1581vs, 1546s, 1517m, 1474m, 1411w, 1080w, 1040w, 991w, 815s, 794s, 737w, 674w and 662m cm^{-1}. *m*/*z* 568 (positive-ion FAB).

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

2,6-Bis[3-(p-*chlorophenyl*)-1-*oxoprop*-2-*enyl*]*pyridine*. 2,6-Diacetylpyridine (2.5 g, 0.015 mol), 4-chlorobenzaldehyde (10.4 g, 0.074 mol) and diethylamine (10 cm^3) were heated to reflux in propan-1-ol (60 cm^3) for 3 h and allowed to cool. The pale yellow crystalline precipitate was filtered off and washed with ice-cold methanol (2.89 g, 47%). IR: 1673s, 1616s, 1592m, 1567m, 1493m, 1408w, 1345m, 1331s, 1205w, 1099w, 1033s, 1017w, 980m, 813w, 800s, 789m, 637w and 491m cm^{-1}. *m*/*z* 407 (EI).

4′,4‴′-*Bis*(p-*chlorophenyl*)-2,2′:6′,2″:6″,2‴:6‴,2‴′-*quinquepyridine* (bcpqpy). 2,6-Bis-[3-(*p*-chlorophenyl)-1-oxoprop-2-enyl]pyridine (0.408 g, 1 mmol), *N*-[1-oxo-2-(2-pyridyl)ethyl]-pyridinium iodide (0.652 g, 2 mmol) and ammonium acetate (4 g) were heated to reflux in a mixture of ethanol (10 cm^3) and glacial acetic acid (1 cm^3) for 24 h and then cooled. The white product was filtered off and recrystallised from boiling toluene to give bcpqpy as an off-white solid (0.31 g, 51%). IR: 1606w, 1582s, 1569s, 1545s, 1496s, 1474w, 1408m, 1383vs, 1092m, 1013w, 819m, 793s and 661w cm^{-1}. *m*/*z* 607 (EI).

2,6-Bis[3-(p-*hydroxyphenyl*)-1-*oxoprop*-2-*enyl*]*pyridine*. 2,6-Diacetylpyridine (2.5 g, 0.015 mol), 4-hydroxybenzaldehyde (9.0 g, 0.074 mol) and diethylamine (10 cm^3) were heated to reflux in propan-1-ol (60 cm^3) for 3 h and allowed to cool. The yellow crystalline precipitate was filtered off and washed with ice-cold methanol (2.97 g, 53%). IR: 1656m, 1588s, 1561s, 1514m, 1444w, 1355w, 1291m, 1244m, 1169m, 1040m, 997w, 984w, 816m and 642w cm^{-1}. *m*/*z* 371 (EI).

4′,4‴′-*Bis*(p-*hydroxyphenyl*)-2,2′:6′,2″:6″,2‴:6‴,2‴′-*quinquepyridine* (bhpqpy). 2,6-bis[3-(*p*-hydroxyphenyl)-1-oxoprop-2-enyl]pyridine (0.375 g, 1 mmol), *N*-[1-oxo-2-(2-pyridyl)ethyl]-pyridinium iodide (0.652 g, 2 mmol) and ammonium acetate (4 g) were heated to reflux in ethanol (10 cm^3) for 24 h and then cooled. The cream product was filtered off (0.4 g, 66%). IR: 3393m(br), 1607s, 1582s, 1548m, 1520vs, 1476w, 1445w, 1391s, 1277m, 1180w, 836w, 819m, 793m, 662w and 570w cm^{-1}. *m*/*z* 571 (EI).

2,6-Bis[3-(p-*dimethylaminophenyl*)-1-*oxoprop*-2-*enyl*]*pyridine*. 2,6-Diacetylpyridine (2.5 g, 0.0015 mol), 4-dimethylamino)benzaldehyde (11.0 g, 0.074 mol) and diethylamine (10 cm^3) were heated to reflux in propan-1-ol (60 cm^3) for 3 h and allowed to cool. The orange crystalline precipitate was filtered off and washed with ice-cold methanol (5.85 g, 92%). IR: 1656m, 1589s, 1567s, 1526s, 1434w, 1368m, 1183m, 1037m, 988w, 813m, 794, 744w, 679w, 640w and 538w cm^{-1}. *m*/*z* 425 (EI).

4′,4‴′-*Bis*(p-*dimethylaminophenyl*)-2,2′:6′,2″:6″,2‴:6‴,2‴′-*quinquepyridine* (bdmpqpy). 2,6-Bis[3-(*p*-dimethylaminophenyl)-1-oxoprop-2-enyl]pyridine (0.43 g, 1 mmol), *N*-[1-oxo-2-(2-pyridyl)ethyl]pyridinium iodide (0.652 g, 2 mmol) and ammonium acetate (4 g) were heated to reflux in propan-1-ol (10 cm^3) for 24 h. The precipitate formed was filtered off from the hot mixture and recrystallised from toluene (0.318 g, 51%). IR: 1601s, 1570s, 1563s, 1520s, 1307m, 1365w, 1209w, 812m and 796w cm^{-1}. *m*/*z* 626 (positive ion FAB).

$[Ni_2L_2(O_2CMe)][PF_6]_3$, $[Cu_2L_2][PF_6]_3$, $[Cu_2L_2(O_2CMe)][PF_6]_3$, *and* $[CoL][PF_6]_2$. The appropriate metal acetate (0.333 mmol) and the appropriate ligand (0.333 mmol) were added to methanol (40 cm^3) and the mixture subjected to ultrasound for 5 min and then heated to reflux until complete dissolution had occurred. An excess of a saturated solution of ammonium hexafluorophosphate in methanol was added, the mixture reduced to half its original volume and then allowed to cool. The product was filtered off and recrystallised either from methanol by slow evaporation or from acetonitrile by diethyl ether diffusion.

The copper complexes were obtained as the dark brown mixed-oxidation-state species [but with short reaction times of the bmtqpy ligand the green dicopper(II) complex was isolated] in 60–80% yields. IR: $[Cu_2(dpqpy)_2][PF_6]_3$, 1614s, 1570w, 1549w, 1475w, 1411w, 1249w, 1014w, 844s, 793w, 765m, 695w, 647w and 559m; $[Cu_2(btqpy)_2][PF_6]_3$, 1607s, 1571w, 1546w, 1474w, 1450w, 1422w, 1250w, 1194w, 1017w, 844s, 791m, 741w and 558m; $[Cu_2(bcpqpy)_2][PF_6]_3$, 1614s, 1586m, 1573m, 1545m, 1500m, 1474m, 1450m, 1424m, 1304m, 1249m, 1168w, 1097m, 1013m, 844s, 792m, 740w and 558m; $[Cu_2(bhpqpy)_2][PF_6]_3$, 3128m(br), 1603s, 1548w, 1522m, 1474w, 1455w, 1411w, 1358w, 1280w, 1239w, 839s, 791m, 741w and 559m; $[Cu_2(bdmpqpy)_2][PF_6]_3$, 1591s, 1569m, 1534m, 1474w, 1447w, 1419w, 1361m, 1209m, 1170m, 844s, 790m, 741w and 558m; $[Cu_2(bmtqpy)_2][PF_6]_3$, 1600s, 1568m, 1539w, 1474w, 1449w, 1413w, 842s, 793m and 558s cm^{-1}.

The nickel(II) complexes were obtained as green crystals in 70–80% yield. IR: $[Ni_2(dpqpy)_2(O_2CMe][PF_6]_3$, 1613s, 1570w, 1551w, 1481w, 1458w, 1443w, 1410w, 1024w, 846s, 794w, 766m, 695m, 652m, 628m and 558m; $[Ni_2(btqpy)_2(O_2CMe)][PF_6]_3$, 1607s, 1574w, 1549w, 1481w, 1452w, 1423w, 1385w, 1027w, 845s, 792m, 741w, 702w and 558m; $[Ni_2(bcpqpy)_2(O_2CMe)][PF_6]_3$, 1614s, 1575w, 1548w, 1484w, 1452w, 1424w, 1097w, 1013w, 849s, 793m, 651m and 559w; $[Ni_2(bhpqpy)_2(O_2CMe)][PF_6]_3$, 3434m(br), 1604s, 1523m, 1483w, 1456w, 1360w, 1281w, 1240w, 1184m, 1080w, 1026w, 845s, 792w and 559m; $[Ni_2(bdmpqpy)_2(H_2O)_2][PF_6]_4$, 1592s, 1570m, 1537m, 1480w, 1421w, 1363m, 1210m, 1169w, 844s, 791m and 559m; $[Ni_2(bmtqpy)_2(O_2CMe)][PF_6]_3$, 1594s, 1569m, 1541m, 1480w, 1450w, 1413w, 846s, 791w and 559m cm^{-1}.

The cobalt(II) complexes were obtained as orange crystals in 50–70% yields. IR: $[Co(dpqpy)(MeCN)_2][PF_6]_2$, 1613s, 1403m, 1082m, 845s, 767m and 559m; $[Co(btqpy)(MeCN)_2][PF_6]_2$, 1607s, 1575m, 1549w, 1483m, 1452w, 1385w, 1015w, 845s, 792m, 701w and 558m; $[Co(bcpqpy)(MeCN)_2][PF_6]_2$, 1614s, 1574m, 1550w, 1483m, 1452w, 1385w, 1095w, 1012m, 845s, 792m and 559m; $[Co(bhpqpy)(MeCN)_2][PF_6]_2$, 3143m(br), 1603s, 1523m, 1481w, 1406m, 1281w, 1241w, 1184w, 1080w, 1023w, 834s and 560m; $[Co(bdmpqpy)(MeCN)_2][PF_6]_2$, 1594s, 1573m, 1535m, 1483m, 1453w, 1425w, 1365m, 1249w, 1210m, 1167w, 1015m, 844s, 792m and 559m; $[Co(bmtqpy)(MeCN)_2][PF_6]_2$, 1597s, 1570m, 1540m, 1482w, 1411w, 845s, 791m and 559m cm^{-1}.

Mass spectroscopic data and elemental analyses results for these complexes are presented in Table 2.

Crystal Structure Determinations of $[Co(bcpqpy)(H_2O)(MeOH)][PF_6]_2$ *and* $[Ni_2(bmtqpy)_2(O_2CMe)][PF_6]_3$.—Orange single crystals of $[Co(bcpqpy)(H_2O)(MeOH)][PF_6]_2$ were obtained by slow evaporation from a methanolic solution of the product from the reaction of cobalt(II) acetate with bcpqpy after the addition of $[NH_4][PF_6]$. Green single crystals of $[Ni_2(bmtqpy)_2(O_2CMe)][PF_6]_3$ were obtained by the diffusion of diethyl ether vapour into an acetonitrile solution of the complex.

Crystal data. $[Co(bcpqpy)(H_2O)(MeOH)][PF_6]_2$. $C_{38}H_{29}Cl_2CoF_{12}N_5O_2P_2$, orange plates, crystal size 0.40 × 0.40 × 0.15 mm, $M = 936.54$, monoclinic, space group $P2_1/a$, $a = 17.441(4)$, $b = 11.765(4)$, $c = 20.402(6)$ Å, $\beta = 105.24(2)°$, $U = 4039$ Å^3, $F(000) = 2028$, $Z = 4$, $D_c = 1.66$ g cm^{-3}, Mo-Kα, radiation (λ = 0.710 73 Å), μ(Mo-Kα) = 7.30 cm^{-1}.

$[Ni_2(bmtqpy)_2(O_2CMe)][PF_6]_3$ + solvent, $C_{60}H_{55}F_{18}N_{10}O_3P_3S_4$, green blocks, crystal size 0.3 × 0.3 × 0.3 mm, $M = 1644.00$, orthorhombic, space group *Pnna*, $a = 16.916(17)$, $b = 25.661(25)$, $c = 16.054(14)$ Å, $U = 6969$ Å^3, $F(000) = 3344$, $Z = 4$, $D_c = 1.57$ g cm^{-3}, μ(Mo-Kα) = 8.30 cm^{-1}.

Data collection and processing. $[Co(bcpqpy)(H_2O)(MeOH)][PF_6]_2$. An orange single crystal was mounted on a glass fibre. All geometric and intensity data were taken from this crystal using an automated four-circle Nicolet R3mV diffractometer equipped with graphite-monochromated Mo-Kα radiation. The ω–2θ technique was used to measure 6036 reflections (5522 unique) in the range $5 \leqslant 2\theta \leqslant 50°$. Three standard reflections (remeasured every 97 scans) showed no significant loss in intensity during data collection. The data were corrected for Lorentz and polarisation effects and an empirical absorption correction applied. The 3346 unique data with $I \geqslant 3.0\sigma(I)$ were used to solve and refine the structure in the monoclinic space group $P2_1/a$.

$[Ni_2(bmtqpy)_2(O_2CMe)][PF_6]_3$. A green single crystal was mounted in a glass capillary and set up to rotate about the *a* axis on a Stoe Stadi2 diffractometer and data were collected *via* variable width ω-scan. Background counts were for 20 s and a scan rate of 0.033° s^{-1} was applied to a width of (1.5 + sin μ/tan θ). 5085 Independent reflections were measured of which 1504 with $I > 2\sigma(I)$ were used in subsequent refinement.

Structural analyses and refinement. The structure of $[Co(bcpqpy)(H_2O)(MeOH)][PF_6]_2$ was solved by Patterson methods and developed by using least-squares refinement and Fourier-difference synthesis. The non-hydrogen atoms were refined anisotropically while hydrogens attached to carbon atoms were placed in idealised positions (C–H 0.96 Å) and assigned a common isotropic thermal parameter (U = 0.08 $Å^2$). The final cycle of least-squares refinement included 559 parameters for 3346 variables and did not shift any parameter by more than 0.004 times its standard deviation. The final *R* values were 0.0851 and 0.0766, and the final Fourier-difference map was featureless with no peaks greater than 0.7 e $Å^{-3}$. Structure solution using SHELXTL-PLUS on a MicroVax II computer.[8] Atomic coordinates are presented in Table 3 and selected bond lengths and angles in Table 4.

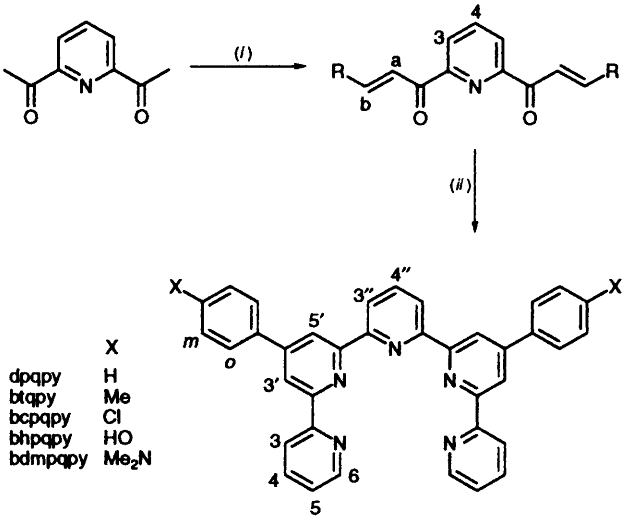
The nickel atoms of $[Ni_2(bmtqpy)_2(O_2CMe)][PF_6]_3$ were located by Patterson methods and all other atoms subsequently located *via* Fourier methods. The structure consists of $[Ni_2(bmtqpy)_2(O_2CMe)]^{3+}$ cations with imposed C_2 symmetry, two independent $[PF_6]^-$ anions, one with imposed C_2 symmetry, and solvent. We were unable to identify the solvent but found four peaks close to a two-fold axis and this could indicate a disordered diethyl ether. Only two of these peaks could be refined; the other two were included in fixed positions. The Ni, P and F atoms were refined anisotropically and the C, N, S and O atoms isotropically. Hydrogen atoms in the cation were included in calculated positions with a common refined thermal parameter. The methyl groups were refined as rigid groups. Hydrogen atoms in the solvent were ignored. The structure was given a weighting scheme of the form $w = 1/[\sigma^2(F) + 0.003F^2]$. The final cycle of least-squares refinement did not shift any parameter by more than 0.1σ. The final *R* values were 0.086 and 0.088, and the final Fourier-difference map had no peaks greater than 0.53 and −0.46 e $Å^{-3}$. Structure solution using SHELX 76[9] and some of our own programs on the Amdahl 5870 at the University of Reading on a MicroVax II computer. Atomic coordinates are presented in Table 5 and selected bond lengths and angles in Table 6.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

2,2′:6′,2″:6″,2‴:6‴,2⁗-Quinquepyridine (qpy) was prepared by the literature method,[5] in which the bis(Mannich) salt obtained from the reaction of 2,6-diacetylpyridine with dimethylammonium chloride and formaldehyde is treated with *N*-[1-oxo-2-(2-pyridyl)ethyl]pyridinium iodide in the presence of an excess of ammonium acetate. Recrystallisation of the ligand from toluene afforded analytically pure material. We have found in the past that it is crucial to use recrystallised samples of oligopyridine ligands for the formation of complexes, as small amounts of pyridine-containing impurities selectively co-ordinate to some metal ions. The structure was confirmed by EI mass spectroscopy (m/z = 387), NMR spectroscopy and elemental analysis.

The 4′,4‴-diaryl-substituted ligands were also prepared by modifications of the literature methods. The first step was the formation of a bis(enone) by the reaction of the appropriate aldehyde (RCHO) with 2,6-diacetylpyridine in the presence of diethylamine. This yielded the bis(enones) in respectable yields. These compounds were all fully characterised by their ^1H NMR, EI or FAB mass, IR spectra and elemental analysis. The principal difficulty associated with the preparation of the bis(enones) is the formation of small quantities of the monoenone species: 2-acetyl-6-(3-aryl-1-oxoprop-2-enyl)pyridines. In general, longer reaction times with a slight excess of the aldehyde prevent the formation of these compounds. It is very important that the monoenones are not present in the later stages of the synthesis as they give rise to substituted 2,2′:6′,2″-terpyridines which compete with the qpy ligands for metal-ion co-ordination. The IR spectra are very characteristic; the bis(enones) exhibit a single carbonyl stretching frequency in the region 1655–1675 cm^{-1}, whereas the monoenones show an additional absorption at around 1700 cm^{-1}. The ^1H NMR spectra of impure samples of the bis(enones) exhibit low-intensity subspectra due to the monoenones. Proton NMR spectroscopic data for the bis(enone) intermediates are presented in Table 1.



Scheme 1 (*i*) RCHO, EtOH, NEt_2H; (*ii*) *N*-[1-oxo-2-(2-pyridyl)ethyl]pyridinium iodide, $[NH_4][O_2CMe]$

The bis(enones) were then converted into the required substituted quinquepyridines by reaction with *N*-[1-oxo-2-(2-pyridyl)ethyl]pyridinium iodide in the presence of an excess of ammonium acetate (Scheme 1).

4′,4‴-Diphenyl-2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine (dpqpy) was prepared as we have described previously.[6] The first step is the formation of the bis(enone) from the reaction of 2,6-diacetylpyridine with benzaldehyde. This yields a yellow crystalline material with a carbonyl stretching frequency at 1671 cm^{-1}. The mass spectrum exhibits a parent ion at m/z 339. The bis(enone) was then converted into dpqpy by the general method. The dpqpy was recrystallised from toluene to remove any unreacted or partially reacted bis(enone) together with any of the more soluble products derived from the monoenone and was obtained in 56% yield. The structure of the product was confirmed by EI mass (m/z 539) and ^1H NMR spectroscopy. The preparation of 4′,4‴-bis(*p*-tolyl)-2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine (btqpy) was successfully achieved in an analogous manner with 4-methylbenzaldehyde. The bis(enone) was a pale yellow crystalline material with a single stretching frequency of the carbonyl at 1670 cm^{-1} in the pure product. Reaction with *N*-[1-oxo-2-(2-pyridyl)ethyl]pyridinium iodide led to the formation of the btqpy. This was recrystallised from toluene to give pure ligand in 82% yield (m/z 568). 4′,4‴-Bis(*p*-chlorophenyl)-2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine (bcpqpy) was prepared in the same manner using 4-chlorobenzaldehyde. The bis(enone) was a pale yellow crystalline material, with ν(C=O) 1673 cm^{-1}, and was converted into the required ligand in 51% yield after recrystallisation from toluene. The structure was confirmed as above (m/z 607, 609). The reaction of 4-hydroxybenzaldehyde with 2,6-diacetylpyridine yielded a yellow bis-

Table 1 Proton NMR data for bis(enones) and oligopyridine ligands in $CDCl_3$ solution. Numbering scheme as indicated in Scheme 1

R in bis(enone)	3	4	a	b	*o*	*m*	
C_6H_4Me-*p*	8.40	8.05	8.40	8.00	7.65	7.25	2.40[a]
C_6H_4Cl-*p*	8.40	8.10	8.35	7.95	7.65	7.42	—
C_6H_4OH-*p*	7.95	7.74	7.95	7.56	7.28	6.57	9.35[b]
$C_6H_4NMe_2$-*p*	8.32	8.02	8.28	7.99	7.67	6.72	1.59[c]

Ligand	6	5	4	3	5′	4′	3′	4″	3″	*o*	*m*	*p*	
terpy	8.70	7.34	7.86	8.63	—	7.97	8.46	—	—				
qtpy	8.72	7.35	7.89	8.67	8.68	8.0	8.48	—	—				
qpy	8.70	7.35	7.88	8.67	8.70	8.01	8.48	8.04	8.72	—	—	—	
dpqpy	8.75	7.37	7.91	8.75	9.0	—	8.75	8.07	8.75	7.95	7.55	7.55	
btqpy	8.77	7.35	7.91	8.70	8.96	—	8.77	8.07	8.72	7.87	7.36	—	2.08[a]
bcpqpy	8.77	7.38	7.91	8.73	8.89	—	8.75	8.07	8.72	7.85	7.51	—	—
bhpqpy	8.78	7.41	8.15	8.74	9.0	—	8.70	8.25	8.74	7.92	7.02	—	10.0[b]
bdmpqpy[d]	8.74	7.35	7.89	8.71	9.01	—	8.73	8.05	8.70	7.93	6.86	—	3.06[c]
bmtqpy	8.70	7.35	7.88	8.65	8.52	—	8.34	8.01	8.67	—	—	—	2.71[e]

[a] Methyl resonance. [b] Hydroxyl resonance. [c] Dimethylamino resonance. [d] In CD_3SOCD_3. [e] Methylthio resonance.

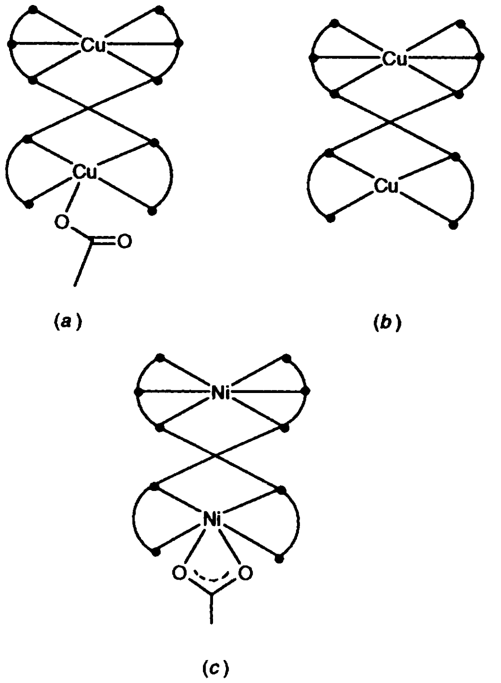


Fig. 1 Schematic representations of the solid-state structures of the cations (*a*) $[Cu_2(qpy)_2(O_2CMe)]^{3+}$, (*b*) $[Cu_2(qpy)_2]^{3+}$ and (*c*) $[Ni_2(qpy)_2(O_2CMe)]^{3+}$

(enone) product with ν(C=O) 1656 cm^{-1}. Conversion of this into 4′,4‴-bis(*p*-hydroxyphenyl)-2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine (bhpqpy) by the standard method gave the pure ligand as a white solid in 66% yield after recrystallisation from dimethylformamide (dmf). The structure was confirmed by ^1H NMR and EI mass spectroscopy (*m*/*z* 571). The reaction of 4-(dimethylamino)benzaldehyde with 2,6-diacetylpyridine yielded a bright orange crystalline product. The IR spectrum of this material exhibited a single ν(C=O) absorption at 1656 cm^{-1}. Conversion of this into the required ligand was only successful in propan-1-ol using freshly recrystallised *N*-[1-oxo-2(2-pyridyl)ethyl]pyridinium iodide. This resulted in the precipitation of yellow 4′,4‴-bis(*p*-dimethylaminophenyl)-2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine (bdmqpy) from the hot solution. Recrystallisation from toluene gave bmpqpy in 51% yield as a yellow solid (*m*/*z* 626).

The details of the ^1H NMR spectra of $CDCl_3$ (CD_3SOCD_3 for bhpqpy) solutions of the free ligands are presented in Table 1. The protons of the aromatic rings were readily assigned by comparison with the spectra of the unsubstituted ligand, 2,2′:6′,2″-terpyridine (terpy)[10,11] and 2,2′:6′,2″:6″,2‴-quaterpyridine (qtpy),[12] along with correlation spectroscopy (COSY) experiments. This allowed unambiguous assignments to be made. In all cases H^5 was the most shielded. The resonance of the 4″ proton is readily identified as a clean triplet. The resonances assigned to $H^{3'}$ and $H^{5'}$ are doublets of identical intensity. Comparisons with the spectra of terpy and qtpy indicate, however, that $H^{5'}$ is more deshielded than $H^{3'}$. The resonances for H^6, H^3 and $H^{3''}$ were overlapping for all the substituted ligands. As expected, substitution of the ligand caused a shift in the positions of the adjacent protons $H^{5'}$ and $H^{3'}$. In all cases these resonances were shifted downfield with respect to their position in the spectrum of the unsubstituted ligand. The effect of changing the *para* group of the phenyl-substituted complexes was, as expected, greatest on the *ortho*- and *meta*-protons of the phenyl ring. Changes in the shifts of the pyridyl resonances of the various aryl-substituted ligands were minimal.

We have previously described the double-helical complexes $[Cu_2(qpy)_2(O_2CMe)][PF_6]_3{\cdot}H_2O$ and $[Cu_2(qpy)_2][PF_6]_3{\cdot}2MeCN$.[13] The complexes with the new ligands were characterised by positive-ion FAB mass spectroscopy, cyclic voltammetry, ESR spectroscopy and X-ray crystallography. The cation in the complex $[Cu_2(qpy)_2(O_2CMe)][PF_6]_3{\cdot}H_2O$ contains two non-equivalent copper(II) centres in a double-helical array of two intertwisted qpy ligands; one copper(II) is six-co-ordinate, bonded to two terpyridyl fragments from each of the two ligands. The second copper(II) is five-co-ordinate, bonded to the remaining two bipyridyl fragments of each of the ligands and an oxygen of a monodentate acetate group [Fig. 1(*a*)]. In the other complex, $[Cu_2(qpy)_2][PF_6]_3{\cdot}2MeCN$, there was one copper(I) and one copper(II) centre. The copper(II) is again six-co-ordinate and bonded to two terpyridyl groups of each of the two qpy ligands, whilst the copper(I) is in a pseudo-tetrahedral environment bonded to the remaining two bipyridyl units [Fig. 1(*b*)]. The preference of the copper(I) centre for a pseudo-tetrahedral site is a strong driving force in the formation of such double-helical complexes with quinquepyridine ligands. We now report a series of analogous dicopper complexes formed with the substituted qpy ligands.

The complexes were prepared by the reaction of a suspension of the ligand with a solution of copper(II) acetate in boiling methanol. The ligands are all insoluble in methanol but dissolve as the reaction proceeds, to give brown solutions. In the case of bmtqpy, short reaction times yield green solutions (as is observed with qpy) but prolonged reaction gives brown solutions. Treatment of these brown solutions with methanolic ammonium hexafluorophosphate results in the deposition of the chocolate-brown complexes $[Cu_2L_2][PF_6]_3$ (L = dpqpy, btqpy, bcpqpy, bhpqpy, bdmpqpy, or bmtqpy). Recrystallisation of these dark brown solids from acetonitrile by diffusion of diethyl ether vapour yielded dark brown crystalline products. The addition of ammonium hexafluorophosphate to the green solution obtained from reaction with bmtqpy precipitated a green material formulated as $[Cu_2(bmtqpy)_2(O_2CMe)][PF_6]_3$.

One of the most useful tools in the characterisation of these complexes has been FAB mass spectroscopy, and in each case high-intensity ions corresponding to $Cu_2L_2(PF_6)_n$ (n = 2, 1 or 0) (L as above) were readily observed. The green complex $[Cu_2(bmtqpy)_2(O_2CMe)][PF_6]_3$ also exhibited ions corresponding to $Cu_2L_2(PF_6)_n$ (n = 2,1 or 0). The presence of peaks corresponding to $M_2L_2^+$, along with the peaks involving various numbers of PF_6 counter ions, and the lack of any acetate fragments, is strong evidence that the brown compounds all have similar structures to that of $[Cu_2(qpy)_2][PF_6]_3$, and that they should be formulated as mixed-valence double-helical complexes. The green complex $[Cu_2(bmtqpy)_2(O_2CMe)][PF_6]_3$ is also double helical and the cation is analogous to that in $[Cu_2(qpy)_2(O_2CMe)][PF_6]_3$. The ^1H NMR spectra of solutions of the brown complexes in acetonitrile were recorded. In all cases the peaks were broad and paramagnetically shifted, and we have been unable to make full assignments; similarities suggested that closely related solution species were present. In each case, three broad resonances were observed at approximately δ 9, 8 and 7.

The brown complexes and green $[Cu_2(bmtqpy)_2(O_2CMe)][PF_6]_3$ are all electrochemically active and exhibit reversible processes in their cyclic voltammograms (MeCN *vs.* Ag-AgCl or Ag–Ag^+ electrodes with ferrocene–ferrocenium as an internal reference, Table 7). The exception to this behaviour was with the complex of bhpqpy where protic reactions involving the hydroxyl groups resulted in irreversible behaviour and a range of adsorption phenomena. In other cases, two reversible metal-centred redox processes are observed. The one to more positive potential involves the $Cu^{II}Cu^{II}$–$Cu^{II}Cu^{I}$ couple and is in the region 0.1–0.2 V, whilst the one to more negative potential involves the $Cu^{II}Cu^{I}$–$Cu^{I}Cu^{I}$ couple and is in the region −0.35 to −0.45 V although this process was not clearly observed for the complex with bdmpqpy. These data, in combination with the similarity in the NMR and mass spectra, all lead us to the conclusion that the binuclear structure of the copper complexes is preserved in solution with all of the substituted ligands.

The ESR spectra of frozen acetonitrile glasses all showed a characteristic signal for copper(II) with the parallel features resolved. This indicated the presence of a copper(II) ion in each of the complexes. For each complex, $g_{\parallel}$ and $A_{\parallel}$ values were 2.010 ± 0.005 and 110 ± 10 Hz respectively. Once again, this provides support for the formation of similar double-helical solution species, regardless of the presence of substituents.

We have previously reported the preparation and structural characterisation of the 2:2 complex $[Ni_2(qpy)_2(O_2CMe)][PF_6]_3\cdot 3MeCN$,[14] which has a very similar structure to that of $[Cu_2(qpy)_2(O_2CMe)][PF_6]_3\cdot H_2O$ discussed above. The two nickel(II) ions are both six-co-ordinate but non-equivalent. One nickel(II) is bonded to a terpyridyl fragment from each qpy. The other is bonded to the two remaining bipyridyl fragments whilst the remaining two sites in its co-ordination sphere are occupied by a bidentate acetate group [Fig. 1(*c*)]. The principal difference between the dinickel(II) and dicopper(II) complexes with qpy lies in the presence of a mono- or bi-dentate acetato ligand. The bidentate acetato group in the dinickel(II) complex is favoured by the ligand-field preference for six-co-ordination in the d^8 ion.

A series of complexes of nickel(II) with the substituted ligands have been prepared and the evidence suggests that the binuclear double helix observed with the parent ligand is conserved in these complexes both in solution and in the solid state. The complexes were prepared by the reaction of nickel(II) acetate with the ligand in boiling methanol. The ligands are essentially insoluble in hot methanol, and the reaction was thus deemed complete when the ligand had dissolved and a clear yellow-green solution had been formed. The reaction time was minimised by ultrasound treatment before heating. The addition of ammonium hexafluorophosphate to the reaction mixtures yielded solid products in shades of cream, through green, to brown. Recrystallising the products by the diffusion of diethyl ether vapour into an acetonitrile solution of the complex, in all cases, yielded fine green crystals. In each case, microanalysis suggested that a formulation $[Ni_2L_2(O_2CMe)][PF_6]_3$ (L = dpqpy, btqpy, bcpqpy, bhpqpy or bmtqpy) was appropriate, with the exception of the complex with bdmpqpy which was formulated as $[Ni_2(bdmpqpy)_2(H_2O)_2][PF_6]_4$; this may be due to the strongly electron-donating nature of this ligand.

Once again, FAB mass spectroscopy proved to be a useful tool in the characterisation of these complexes. In each case, ions corresponding to binuclear Ni_2L_2 (L as above) fragments were observed in the FAB mass spectrum, as indicated in Table 2. The presence of peaks corresponding to $M_2L_2^+$, along with the fragmentation peaks showing loss of a counter ion or an acetate from the parent complex, is strong evidence for the products having similar solid-state structures to that of the structurally characterised complex $[Ni_2(qpy)_2(O_2CMe)][PF_6]_3$.[14]

The complexes are paramagnetic and solution, Evans method, determination of the magnetic moment[15] indicated μ_{eff} of 4.2 ± 0.3 for the binuclear formulation. The ^1H NMR spectra of the complexes in acetonitrile were recorded. All of the resonances are paramagnetically shifted and broadened. The NMR spectra of paramagnetic nickel(II) complexes have been subject to detailed studies over a number of years.[16] With our complexes, all of the resonances are shifted downfield and all coupling information is lost. The broadening is not so marked as with the copper complexes, however, and the chemical shift range is considerably greater. Thus separate peaks were mostly still distinguishable and chemical shift data are presented in Table 8. The number of peaks observed indicates that the bipy and terpy portions of the ligand are in different environments and this is consistent with the $[Ni_2L_2(O_2CMe)]^{3+}$ (L = dpqpy, btqpy, bcpqpy, bhpqpy, bdmpqpy, or bmtqpy) species being conserved in solution. Also notable is the observation of remarkably similar spectra in each case, *and* the observation of more resonances than are required for a symmetrical mononuclear structure in *every* case. Although we are unable fully to assign the spectra as a result of the lack of observable coupling, partial assignments may be made. Comparisons between the ^1H NMR spectra of the nickel(II) complexes of the substituted terpyridines [2,2′:6′,2″-terpyridine (terpy), 4′-phenyl-2,2′:6′,2″-terpyridine (pterpy) and 4′-(*p*-hydroxyphenyl)-2′,2″:6′,2″-terpyridine (hpterpy)][17,18] and of the complexes of the quinquepyridines indicates a number of conserved resonances. These can thus be attributed to the protons on the terminal ring of the terpyridyl fragment (T) of the quinquepyridine and half of the adjacent ring. It is possible fully to assign $H^{4'}$ and the *p*-proton of the phenyl ring by comparison between terpy, pterpy and hpterpy, and similarly these protons can be identified in the spectra of the quinquepyridine complexes. Resonances corresponding to the bipyridine fragment (B) of the quinquepyridine and the acetate could be identified by comparison with the spectra of the complexes $[Ni_2L_2(O_2CMe)_2][PF_6]_2$ [L = 1,3-bis(2,2′-bipyridin-6-yl)benzene (bbpbz) or 1,3-bis(4′-methylthio-2,2′-bipyridin-6-yl)benzene] (bmtbpbz) in which both nickel atoms are co-ordinated by two bipyridine fragments and a bidentate acetate.[19] Again these resonances were conserved. The remaining four resonances (X) thus correspond to the remaining proton on the central ring of the terpyridyl fragment and $H^{3'''}$, $H^{4'''}$ and $H^{5'''}$.

The nickel complexes are redox active, and cyclic voltammetric studies were performed in acetonitrile against Ag–AgCl or Ag–Ag^+ electrodes with ferrocene–ferrocenium as an

Table 2 Elemental analysis and positive-ion FAB mass spectroscopic data for metal complexes of qpy ligands

Complex	*M*	Analysis (%)* C	H	N	*m*/*z*
$[Cu_2(dpqpy)_2][PF_6]_3\cdot MeCN$	1680	54.35 (54.30)	3.30 (3.15)	9.10 (9.15)	1494, $Cu_2L_2(PF_6)_2$; 1351, $Cu_2L_2(PF_6)$
$[Cu_2(btqpy)_2][PF_6]_3\cdot MeCN$	1736	55.30 (55.35)	3.70 (3.60)	9.65 (9.45)	1554, $Cu_2L_2(PF_6)_2$; 1408, $Cu_2L_2(PF_6)$
$[Cu_2(bcpqpy)_2][PF_6]_3$	1777	49.85 (49.95)	2.50 (2.60)	7.95 (7.90)	1634, $Cu_2L_2(PF_6)_2$; 1489, $Cu_2L_2(PF_6)$
$[Cu_2(bhpqpy)_2][PF_6]_3\cdot 3H_2O$	1757	47.70 (50.55)	2.85 (3.20)	8.20 (7.95)	1560, $Cu_2L_2(PF_6)_2$; 1414, $Cu_2L_2(PF_6)$
$[Cu_2(bdmpqpy)_2][PF_6]_3\cdot H_2O$	1829	52.45 (53.80)	3.95 (3.95)	11.80 (10.70)	1668, $Cu_2L_2(PF_6)_2$; 1523, $Cu_2L_2(PF_6)$
$[Cu_2(bmtqpy)_2][PF_6]_3$	1519	42.40 (42.65)	3.05 (2.75)	9.50 (9.20)	1376, $Cu_2L_2(PF_6)_2$; 1231, $Cu_2L_2(PF_6)$
$[Ni_2(dpqpy)_2(O_2CMe)][PF_6]_3\cdot 2H_2O$	1726	52.75 (52.85)	3.10 (3.30)	8.10 (8.10)	1545, $Ni_2L_2(O_2CMe)(PF_6)_2$; 1486, $Ni_2L_2(PF_6)_2$
$[Ni_2(btqpy)_2(O_2CMe)][PF_6]_3\cdot H_2O$	1764	54.25 (54.40)	3.70 (3.55)	7.80 (7.95)	1602, $Ni_2L_2(O_2CMe)(PF_6)_2$; 1543, $Ni_2L_2(PF_6)_2$
$[Ni_2(bcpqpy)_2(O_2CMe)][PF_6]_3\cdot H_2O$	1846	49.65 (49.40)	2.90 (2.75)	7.55 (7.60)	1625, $Ni_2L_2(PF_6)_2$; 1480, $Ni_2L_2(PF_6)$
$[Ni_2(bhpqpy)_2(O_2CMe)][PF_6]_3\cdot 2H_2O$	1758	50.90 (51.90)	3.00 (3.25)	7.70 (7.95)	1402, $Ni_2L_2(PF_6)$; 1257, Ni_2L_2
$[Ni_2(bdmpqpy)_2(H_2O)_2][PF_6]_4$	1984	49.20 (49.60)	3.70 (3.75)	10.00 (9.90)	1824, $Ni_2L_2(H_2O)(PF_6)_3$; 1676, $Ni_2L_2(H_2O)(PF_6)_2$
$[Ni_2(bmtqpy)_2(O_2CMe)][PF_6]_3\cdot 2H_2O$	1606	41.55 (41.85)	2.85 (3.05)	8.50 (8.70)	1426, $Ni_2L_2(O_2CMe)(PF_6)_2$; 1280, $Ni_2L_2(O_2CMe)(PF_6)$
$[Co(dpqpy)(MeCN)_2][PF_6]_2\cdot H_2O$	988	50.15 (49.80)	3.25 (3.35)	10.30 (9.20)	744, $CoL(PF_6)$; 598, CoL
$[Co(btqpy)(MeCN)_2][PF_6]_2\cdot 0.5MeCN$	1018.5	51.65 (51.85)	3.50 (3.60)	10.35 (10.30)	772, $CoL(PF_6)$; 626, CoL
$[Co(bcpqpy)(MeCN)_2][PF_6]_2\cdot MeCN$	1080	47.70 (47.80)	3.00 (2.95)	10.50 (10.35)	811.5, $CoL(PF_6)$; 666, CoL
$[Co(bhpqpy)(MeCN)_2][PF_6]_2\cdot H_2O$	1020	47.15 (48.25)	3.10 (3.25)	9.95 (9.60)	775, $CoL(PF_6)$; 630, CoL
$[Co(bdmpqpy)(MeCN)_2][PF_6]_2\cdot 2MeOH$	1120	49.90 (50.35)	4.10 (4.40)	10.75 (11.25)	829, $CoL(PF_6)$; 684, CoL
$[Co(bmtqpy)(MeCN)_2][PF_6]_2$	910	40.50 (40.90)	2.70 (2.95)	8.90 (10.75)	683, $CoL(PF_6)$; 598, CoL

* Calculated values in parentheses.

internal reference. In each case, no oxidation waves were observed at positive potentials up to +1.5 V. A number of reduction waves appeared at negative potentials. The pattern of these waves was the same as those observed for the complexes with qpy, and may be assigned as previously described.[6,14] This similarity also suggests that the structures of the complexes with substituted ligands were the same as those for the complex with qpy, and also that the double-helical structure persists in solution. The potentials and assignments are indicated in Table 7.

In order to confirm the formation of double-helical structures for these nickel complexes we have determined the crystal and molecular structure of the complex $[Ni_2(bmtqpy)_2(O_2CMe)][PF_6]_3$. We chose this complex, as such alkylthio-substituted ligands had previously been shown to give rise to mononuclear complexes upon reaction with cobalt(II) in the presence of chloride,[20] and we had considered that this was a consequence of the presence of halide ion.[21] The lattice consists of discrete double-helical $[Ni_2(bmtqpy)_2(O_2CMe)]^{3+}$ cations, hexafluorophosphate anions and solvent molecules; the structure of one of the two enantiomers of the cation is presented in Figs. 2(*a*) and 2(*b*). Each nickel(II) centre is six-co-ordinate; Ni(1) is in an N_6 environment and is co-ordinated to a terdentate terpyridyl functionality from each of two bmtqpy ligands whilst Ni(2) is in an N_4O_2 environment generated by the remaining bipyridyl donor set of each of the two bmtqpy ligands and a bidentate acetate group. The two nickel atoms lie on a C_2 symmetry axis, as do the two carbon atoms of the co-ordinated acetate ligand. The structure closely resembles that found in $[Ni_2(qpy)_2(O_2CMe)][PF_6]_3$[14] and $[Co_2(qpy)_2(O_2CMe)][PF_6]_3$.[21] The Ni–N distances are all in the expected range 1.972(12)–2.221(12) Å, with the large variations resulting from the distortions consequent upon the helically distorted ligand. As expected, the 'terpyridyl' groups show short interactions [Ni(1)–N(21) 1.972(12) Å] to the central pyridine ring and longer [Ni(1)–N(12) 2.136(19), Ni(1)–N(31) 2.221(12) Å] distances to the 'terminal' pyridines. The geometry about Ni(1) is highly distorted, whereas that about Ni(2) is closer to octahedral, being dominated by the small bite of the bidentate acetate ligand.

The helication is principally a result of the twisting of 45.5° of the bmtqpy ligand about the interannular C–C bond connecting the 'terpyridine' and the 'bipyridine' parts. This twisting is somewhat smaller than is observed in the parent qpy complex (58–60°). The sequential interplanar angles within the bmtqpy ligand are 2.6, 26.3, 45.5 and 15.6°. The Ni(1) ··· Ni(2) distance of 4.44 Å is essentially identical to that of 4.45 Å observed in $[Ni_2(qpy)_2(O_2CMe)][PF_6]_3$.[14] As observed in previous double-helical complexes of qpy ligands, the approximately planar pyridine rings of the two ligands exhibit short contacts (Fig. 3). The introduction of the methylthio substituents has little effect upon the overall structure of the cation.

We have also shown that the reaction of qpy with cobalt(II) acetate leads to the formation of a compound which contains dinuclear double-helical $[Co_2(qpy)_2(O_2CMe)]^{3+}$ cations in the solid state.[21] These double-helical cations were nearly identical to those of the corresponding nickel(II) complexes discussed above. In contrast, the reaction of 4′,4‴-bis(*n*-propylthio)-2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine (bptqpy) with cobalt(II)

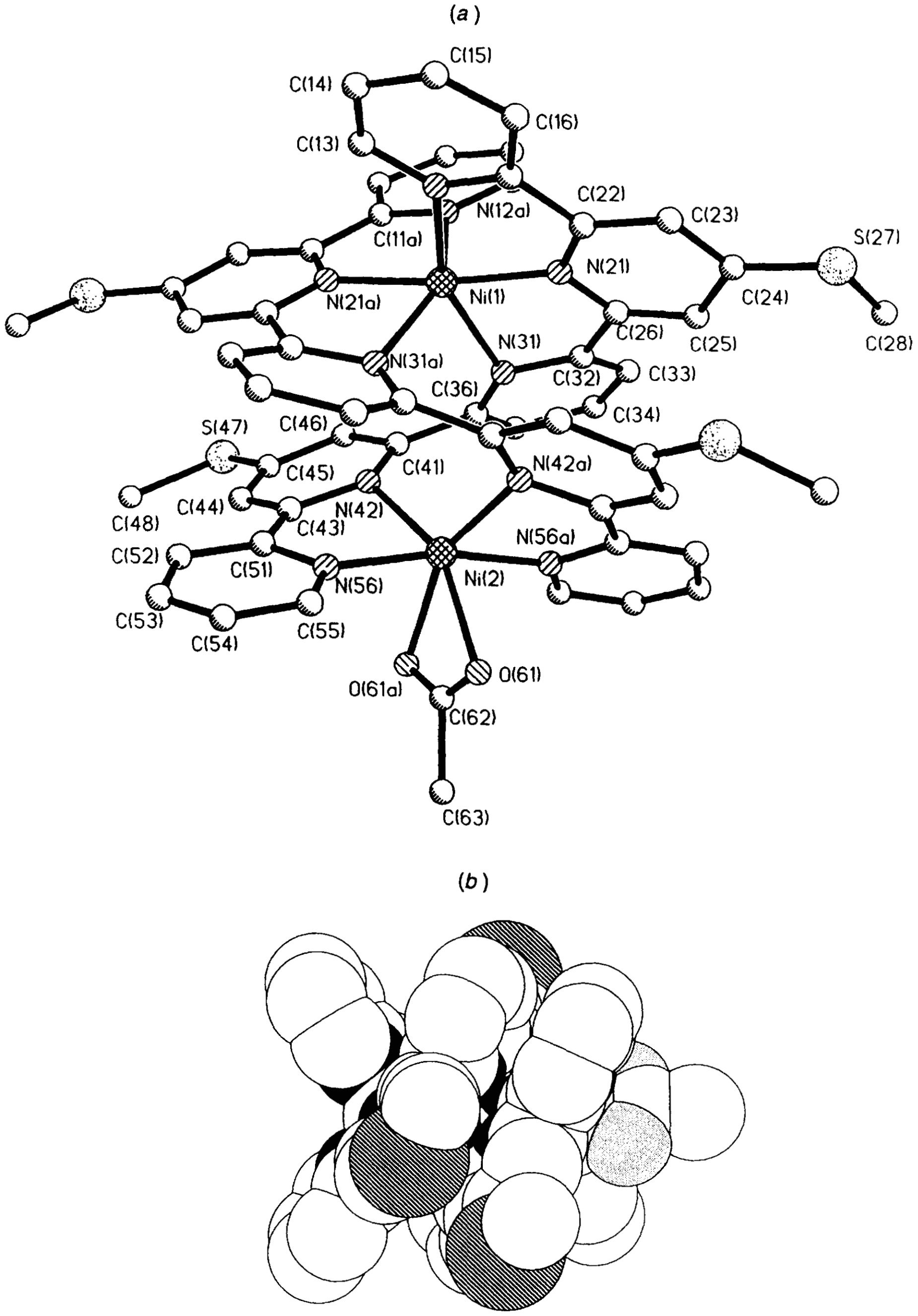


Fig. 2 (*a*) Crystal and molecular structure of one of the two enantiomers of the binuclear double-helical cation $[Ni_2(bmtqpy)_2(O_2CMe)]^{3+}$ present in the lattice of $[Ni_2(bmtqpy)_2(O_2CMe)][PF_6]_3$ + solvent showing the numbering scheme adopted and (*b*) a space-filling representation of the same cation

chloride was known to yield the mononuclear seven-coordinate complex $[Co(bptqpy)Cl_2]$.[20] We now describe a systematic study of the behaviour of cobalt(II) with substituted quinquepyridines.

On heating suspensions of any of the substituted ligands with a solution of cobalt(II) acetate in methanol, the ligands dissolve to yield orange-brown solutions of cobalt(II) complexes. Treatment of these solutions with methanolic ammonium hexafluorophosphate results in the precipitation of pale orange solids which can be recrystallised from acetonitrile by the diffusion of diethyl ether vapour or from hot methanol to yield good-quality crystals. These complexes are paramagnetic and the solution-phase Evans method determination by NMR spectroscopy gave magnetic moments μ_{eff} 4.1 ± 0.3.[15]

The FAB mass spectra of all the complexes with substituted qpy ligands exhibit peaks assigned to $CoL(PF_6)$ (L = dpqpy, btqpy, bcpqpy, bhpqpy, bdmpqpy, or bmtqpy). This is in contrast to the complex of qpy which exhibits high-intensity peaks assigned to dinuclear species. This is circumstantial evidence for the presence of mononuclear species, although there are a number of examples of helicates which are mononuclear in the solid state but which exhibit binuclear ions in the mass spectrum [for example, silver(I)–qpy complexes] and of complexes which are binuclear in the solid state but which only exhibit very low-intensity binuclear peaks in their FAB mass spectra.

The electrochemical behaviour of cobalt(II) complexes with qpy had long puzzled us. The cyclic voltammetry of $[Co_2(qpy)_2(O_2CMe)][PF_6]_3$ was complicated and a total of ten processes was detected. This complexity was also observed for the substituted complexes and details are presented in Table 7. The principal difficulty we had was in the oxidation of these

Table 3 Atomic coordinates (× 10^4) for $[Ni_2(bmtqpy)_2(O_2CMe)][PF_6]_3$

Atom	*x*	*y*	*z*
Ni(1)	2 686(2)	2 500^a	7 500^a
Ni(2)	5 309(2)	2 500^a	7 500^a
C(11)	1 851(12)	2 762(7)	5 951(12)
N(12)	1 883(11)	2 930(8)	6 737(12)
C(13)	1 527(12)	3 394(8)	6 936(12)
C(14)	1 121(14)	3 692(9)	6 396(13)
C(15)	1 105(16)	3 520(10)	5 580(16)
C(16)	1 431(12)	3 053(8)	5 329(12)
N(21)	2 627(8)	2 075(5)	6 478(7)
C(22)	2 259(10)	2 264(6)	5 812(9)
C(23)	2 256(12)	2 015(8)	5 035(14)
C(24)	2 650(10)	1 540(7)	4 952(11)
C(25)	3 043(10)	1 323(7)	5 792(10)
C(26)	2 986(9)	1 626(5)	6 439(8)
S(27)	2 680(4)	1 229(2)	4 062(4)
C(28)	3 052(15)	618(8)	4 321(15)
N(31)	3 533(7)	1 857(5)	7 747(7)
C(32)	3 377(10)	1 465(6)	7 225(9)
C(33)	3 490(12)	958(8)	7 399(14)
C(34)	3 826(11)	835(8)	8 135(12)
C(35)	4 045(14)	1 247(8)	8 693(14)
C(36)	3 920(12)	1 721(7)	8 446(11)
C(41)	4 227(9)	2 167(7)	8 911(10)
N(42)	4 621(8)	2 566(6)	8 579(8)
C(43)	4 889(10)	2 975(7)	9 040(11)
C(44)	4 785(11)	3 010(8)	9 842(11)
C(45)	4 442(12)	2 617(8)	10 239(11)
C(46)	4 120(12)	2 194(8)	9 797(12)
S(47)	4 322(4)	2 538(3)	11 315(4)
C(48)	4 753(17)	3 166(11)	11 637(18)
C(51)	5 217(10)	3 404(7)	8 528(10)
C(52)	5 327(11)	3 880(7)	8 880(11)
C(53)	5 681(12)	4 240(9)	8 341(14)
C(54)	5 847(11)	4 112(8)	7 562(15)
C(55)	5 727(12)	3 619(8)	7 271(13)
N(56)	5 426(8)	3 280(5)	7 741(8)
O(61)	6 404(9)	2 558(7)	6 814(9)
C(62)	6 692(17)	2 500^a	7 500^a
C(63)	7 587(23)	2 500^a	7 500^a
P(71)	0^a	5 000^a	5 000^a
F(72)	430(8)	365(6)	596(9)
F(73)	571(9)	140(7)	−673(10)
F(74)	−526(10)	478(6)	−140(9)
P(81)	4 053(5)	5 493(3)	8 821(5)
F(82)	4 145(13)	4 917(7)	8 797(16)
F(83)	3 894(12)	6 104(5)	8 885(11)
F(84)	4 375(14)	5 546(11)	7 970(10)
F(85)	3 653(10)	5 506(7)	9 680(13)
F(86)	4 879(8)	5 592(8)	9 247(11)
F(87)	3 205(12)	5 447(9)	8 482(16)
O(100)	3 882(22)	810(13)	1 975(20)
C(101)	3 132(29)	1 215(17)	1 307(28)
C(102)^b	2 562	1 013	498
C(103)^b	2 883	255	2 574

^{a} Parameter fixed. ^{b} All atom coordinates fixed.

Table 4 Selected bond lengths (Å) and angles (°) for $[Ni_2(bmtqpy)_2(O_2CMe)][PF_6]_3$

Ni(1)–N(12)	2.136(19)	Ni(2)–N(42)	2.092(13)
Ni(1)–N(21)	1.972(12)	Ni(2)–N(56)	2.047(14)
Ni(1)–N(31)	2.221(12)	Ni(2)–O(61)	2.160(15)
N(12)–Ni(1)–N(21)	77.1(6)	N(42)–Ni(2)–N(56)	79.5(5)
N(12)–Ni(1)–N(31)	153.7(5)	N(42)–Ni(2)–O(61)	153.2(5)
N(21)–Ni(1)–N(31)	76.7(5)	N(56)–Ni(2)–O(61)	86.9(6)
N(12)–Ni(1)–N(12^I)	101.1(6)	N(42)–Ni(2)–N(56^I)	106.8(6)
N(12)–Ni(1)–N(21^I)	99.2(6)	N(42)–Ni(2)–O(61^I)	93.5(5)
N(12)–Ni(1)–N(31^I)	85.6(6)	N(56)–Ni(2)–N(56^I)	168.9(6)
N(21)–Ni(1)–N(21^I)	174.2(6)	N(56)–Ni(2)–O(61^I)	83.6(6)
N(21)–Ni(1)–N(31^I)	107.1(5)	O(61)–Ni(2)–O(61^I)	61.9(6)
N(31)–Ni(1)–N(31^I)	99.6(5)	N(42)–Ni(2)–N(42^I)	112.5(5)

Symmetry operation: I $x, \frac{1}{2} - y, \frac{3}{2} - z$.

complexes. Although some ill defined oxidation processes had been observed for the complex with qpy, no such processes were observable for the complexes of the substituted ligands. The solid-state structure of $[Co_2(qpy)_2(O_2CMe)][PF_6]_3$ revealed the presence of a distorted-octahedral cobalt(II) centre in a strong-field N_6 environment; a cobalt in such an environment is expected to be readily oxidised to cobalt(III). The similarity of the electrochemical data suggested that similar solution species were obtained with the substituted ligands.

In order further to elucidate the structures of these complexes, we have determined the crystal and molecular structure of a cobalt(II) complex of bcpqpy. Slow cooling of the solution obtained from the reaction of bcpqpy with cobalt(II) acetate in methanol after the addition of $[NH_4][PF_6]$ gave good-quality red crystals of a complex $[Co(bcpqpy)(H_2O)(MeOH)][PF_6]_2$; the crystal and molecular structure of one of the two enantiomers present in the unit cell is presented in Fig. 4(*a*), and a space-filling representation in Fig. 4(*b*). The cation is mononuclear, with the bcpqpy acting as a pentadentate ligand with a shallow helical twist about the equatorial plane of a pentagonal-bipyramidal metal centre. The two axial sites are occupied by a water molecule and a methanol molecule. The helical twisting of the bcpqpy ligand minimises the interactions which would occur between the two terminal rings of the ligand in a completely planar configuration. The helical configuration is achieved by a series of individual twistings about interannular C–C bonds between adjacent pyridine rings (1/2, 17.7; 2/3, 15.0; 3/4, 6.4; 4/5, 12.4°; rings numbered according to the nitrogen atoms they contain). The chlorophenyl substituents are not coplanar with the pyridine rings to which they are attached, but are skewed (2/cp, 26.4; 4/cp, 18.8°). These are similar to the pyridine/aryl twistings which we have previously observed in the complex $[Ni(pterpy)_2]Cl_2$.[15] The PF_6 counter ions do not

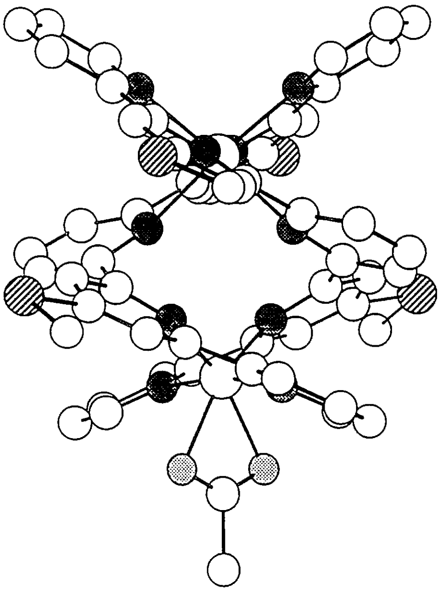


Fig. 3 An alternative representation of the cation $[Ni_2(bmtqpy)_2(O_2CMe)]^{3+}$ emphasising the stacking interactions between the two ligands

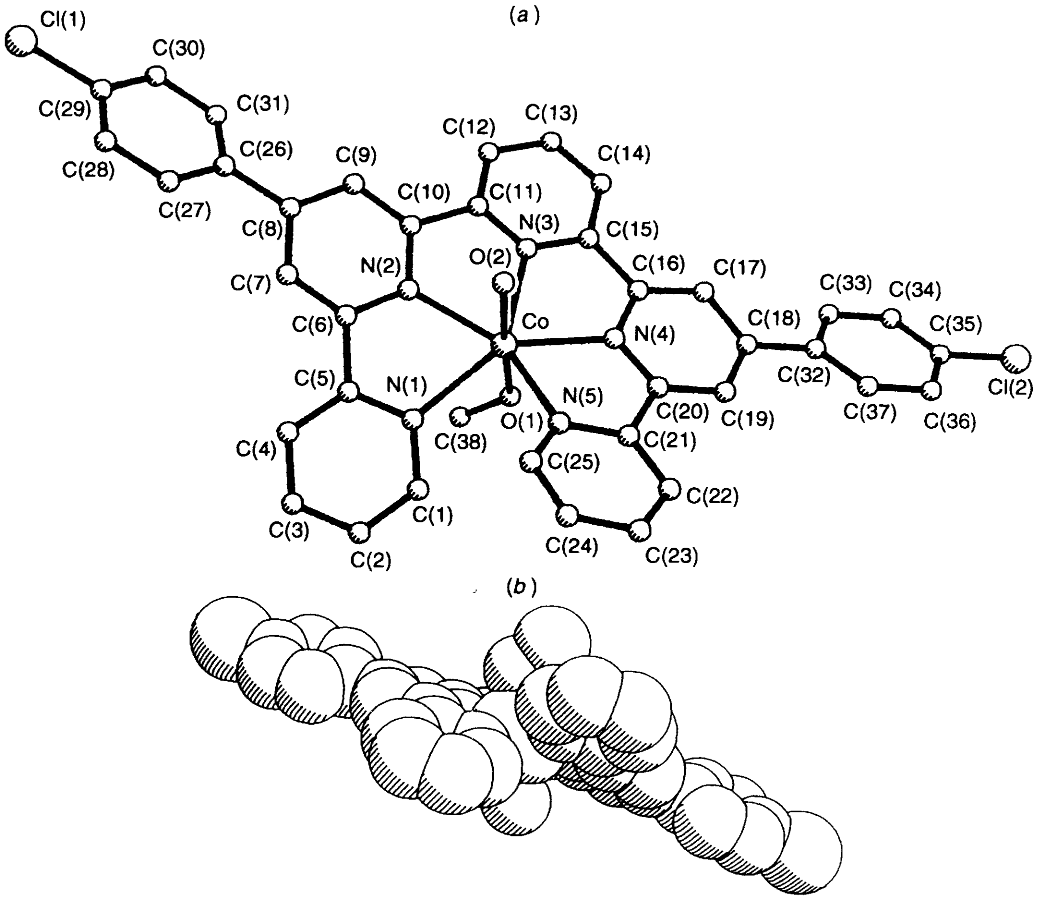


Fig. 4 (*a*) Crystal and molecular structure of one of the two enantiomers of the mononuclear cation $[Co(bcpqpy)(H_2O)(MeOH)]^{2+}$ present in the lattice of $[Co(bcpqpy)(H_2O)(MeOH)][PF_6]_2$ showing the numbering scheme adopted and (*b*) a space-filling representation of the same cation

Table 5 Atomic coordinates (× 10^4) for $[Co(bcpqpy)(H_2O)(MeOH)][PF_6]_2$

Atom	*x*	*y*	*z*
Co	529(1)	1432(1)	2200(1)
Cl(1)	1756(2)	−5061(3)	6144(2)
Cl(2)	353(2)	3685(3)	−3045(2)
N(1)	670(5)	2321(8)	3220(4)
N(2)	1070(5)	250(7)	3014(4)
N(3)	1084(5)	2(7)	1774(4)
N(4)	354(5)	1721(7)	1116(4)
N(5)	−429(5)	2744(8)	1856(4)
O(1)	1591(5)	2470(8)	2221(4)
O(2)	−508(4)	350(6)	2118(4)
C(1)	631(7)	3461(10)	3309(5)
C(2)	756(7)	3948(10)	3945(6)
C(3)	909(9)	3253(11)	4515(6)
C(4)	956(8)	2101(11)	4418(6)
C(5)	853(7)	1661(9)	3771(5)
C(6)	991(6)	443(9)	3652(5)
C(7)	1108(6)	−415(9)	4128(5)
C(8)	1307(6)	−1490(9)	3976(5)
C(9)	1410(6)	−1673(10)	3327(5)
C(10)	1292(6)	−784(9)	2865(5)
C(11)	1378(7)	−881(9)	2163(5)
C(12)	1776(6)	−1738(9)	1933(5)
C(13)	1816(7)	−1704(10)	1268(6)
C(14)	1486(6)	−823(9)	859(6)
C(15)	1121(6)	54(10)	1126(5)
C(16)	739(6)	1078(8)	759(5)
C(17)	743(7)	1348(10)	93(5)
C(18)	367(7)	2334(9)	−203(5)
C(19)	−48(6)	2965(9)	162(5)
C(20)	−51(6)	2624(9)	816(5)
C(21)	−524(6)	3191(9)	1229(5)
C(22)	−1058(7)	4063(10)	984(6)
C(23)	−1533(8)	4451(11)	1372(6)
C(24)	−1478(7)	3965(11)	1995(6)
C(25)	−921(7)	3139(10)	2210(6)
C(26)	1409(7)	−2389(10)	4510(5)
C(27)	1018(8)	−2306(11)	5019(6)
C(28)	1132(9)	−3138(11)	5518(6)
C(29)	1623(7)	−4022(10)	5503(5)
C(30)	2014(7)	−4125(10)	5011(6)
C(31)	1911(7)	−3275(10)	4520(6)
C(32)	361(7)	2681(9)	−910(5)
C(33)	938(7)	2242(10)	−1207(5)
C(34)	925(8)	2569(10)	−1872(6)
C(35)	355(8)	3285(10)	−2219(6)
C(36)	−215(8)	3744(11)	−1935(5)
C(37)	−213(7)	3411(10)	−1283(5)
C(38)	2217(8)	2722(14)	2772(7)
P(1)	1338(3)	485(3)	6376(2)
F(1)	638(6)	319(9)	5701(4)
F(2)	1482(6)	1728(7)	6130(5)
F(3)	697(5)	964(7)	6731(4)
F(4)	1999(6)	673(10)	7018(5)
F(5)	1935(5)	−25(8)	5990(5)
F(6)	1165(6)	−723(7)	6596(4)
P(2)	7327(2)	627(4)	783(2)
F(7)	7086(6)	1185(9)	66(4)
F(8)	8222(6)	939(10)	844(5)
F(9)	7508(7)	−494(9)	170(6)
F(10)	7612(7)	35(13)	1464(5)
F(11)	7180(7)	1750(9)	1101(5)
F(12)	6460(6)	258(10)	668(6)

interact directly with the metal centre, but a short contact (2.89 Å) between the methanol oxygen atom O(1) and one of the fluorine atoms [F(11)] is indicative of an O–H • • • F hydrogen bond. As expected, the Co–N contacts to the terminal rings are significantly longer than those to the 'inner' rings, but the Co–N distances are otherwise unremarkable. This is due to the strain imposed on the ligand by co-ordinating to the small metal centre. The structure very closely resembles that of [Co-(bptqpy)Cl_2].[20]

The above results presented something of a paradox. The qpy and bcpqpy complexes possessed different solid-state structures, but they exhibited remarkably similar solution-state electrochemical properties. The FAB mass spectra of the complexes suggested that all of the substituted ligands gave rise to mononuclear species. However, they were routinely recorded using 3-nitrobenzyl alcohol as a matrix, which may be regarded as a pseudo-solution technique in which the matrix acts as a donor solvent.

In order further to understand the natures of these complexes we have investigated their ^1H NMR spectra in acetonitrile solution. In all cases the spectra exhibited large paramagnetic shifts. The peaks were broadened but well separated (Table 9). The first feature of note is the observation that solutions of all the complexes, including the solid-state double-helical complex $[Co_2(qpy)_2(O_2CMe)][PF_6]_3$ [Fig. 5(*b*)] and the solid-state single-helical complex $[Co(bcpqpy)(H_2O)(MeOH)][PF_6]_2$ [Fig. 5(*a*)], in CD_3CN exhibit very similar spectra. The only differences in the spectra result from the replacement of the $H^{4',4'''}$ protons by aryl groups on passing from the qpy to the aryl-substituted ligands and from the differences between these substituents. In all cases, the number of resonances indicates that the ligand is symmetrical about the central pyridine ring on the NMR time-scale; the qpy and bmtqpy complexes exhibit nine resonances, the dpqpy and btqpy complexes twelve, and the others eleven. This is only compatible with the solution species possessing the single-helical structure, presumably with axial acetonitrile ligands (Scheme 2). The lowest-field resonances (δ 134–135) are assigned to $H^{6'}$. A resonance at δ 19.0 may readily be assigned to $H^{4''}$ as it is of half the intensity as that of the others. The resonance at δ 19.8 in the spectrum of the qpy complex may be assigned to $H^{4'}$ as it is not present in the other spectra. The resonances of the aromatic substituents may be reliably assigned by comparison of the various spectra. The remaining resonances associated with the pyridine rings are found at characteristic chemical shifts, and are independent of the nature of the substituted ligand (δ 81.3, 77.9, 75.6, 69.9 and 50.4). Attempts to assign these resonances by COSY or single-frequency decoupling were unsuccessful.

The formation of these mononuclear species explains why a facile Co^{II}–Co^{III} oxidation is not observed in the electrochemistry: the solution species is seven-co-ordinate pentagonal

Table 6 Selected bond lengths (Å) and angles (°) for $[Co(bcpqpy)(H_2O)(MeOH)[PF_6]_2$

Co–N(1)	2.283(8)	Co–N(2)	2.180(8)
Co–N(3)	2.229(9)	Co–N(4)	2.179(8)
Co–N(5)	2.247(9)	Co–O(1)	2.209(9)
Co–O(2)	2.183(8)		
N(1)–Co–N(2)	71.2(3)	N(1)–Co–N(3)	138.4(3)
N(2)–Co–N(3)	70.7(3)	N(1)–Co–N(4)	143.8(3)
N(2)–Co–N(4)	142.1(3)	N(3)–Co–N(4)	71.4(3)
N(1)–Co–N(5)	82.2(3)	N(2)–Co–N(5)	144.4(3)
N(3)–Co–N(5)	139.4(3)	N(4)–Co–N(5)	71.4(3)
N(1)–Co–O(1)	80.8(3)	N(2)–Co–O(1)	98.4(3)
N(3)–Co–O(1)	88.7(3)	N(4)–Co–O(1)	80.0(3)
N(5)–Co–O(1)	100.2(3)	N(1)–Co–O(2)	103.1(3)
N(2)–Co–O(2)	82.6(3)	N(3)–Co–O(2)	88.0(3)
N(4)–Co–O(2)	96.9(3)	N(5)–Co–O(2)	81.0(3)

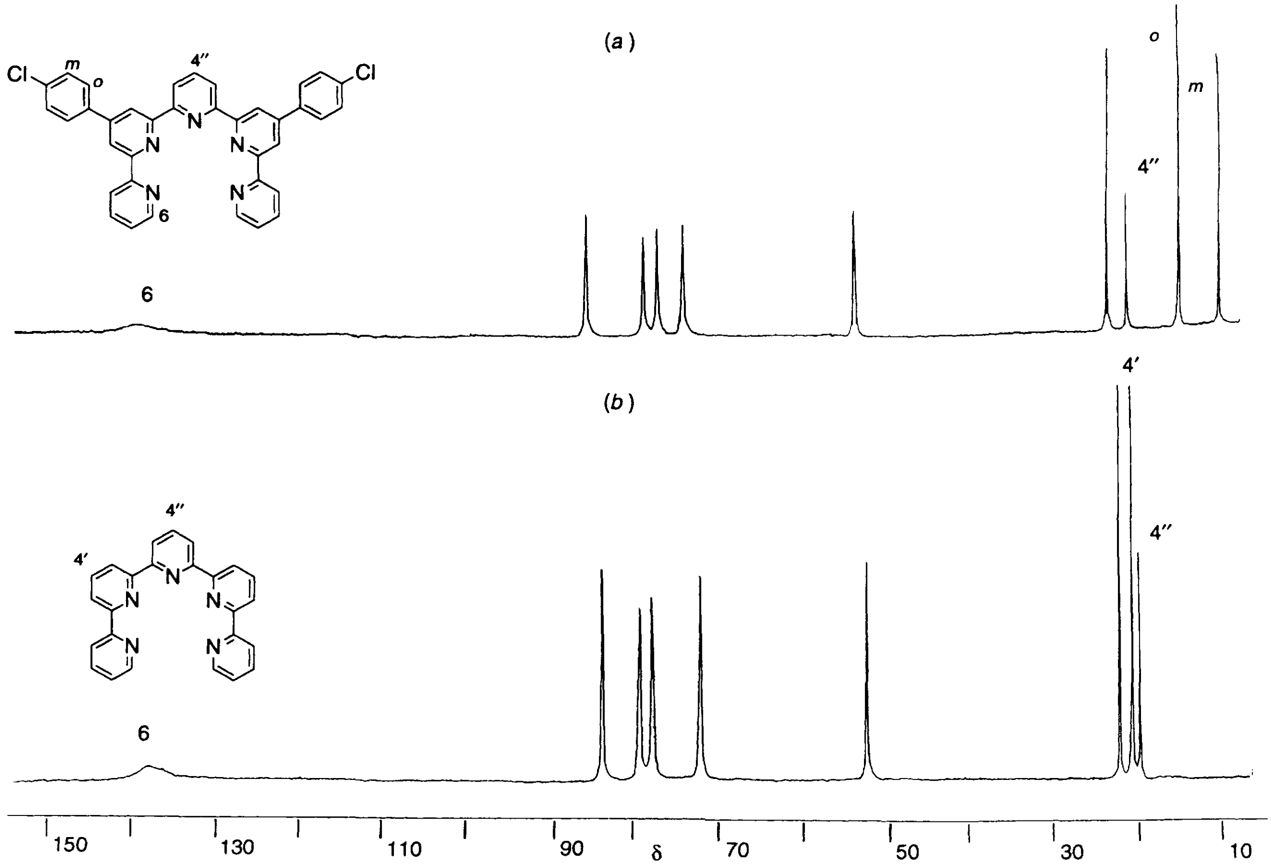


Fig. 5 Proton NMR spectra of CD_3CN solutions of (*a*) $[Co(bcpqpy)(H_2O)(MeOH)][PF_6]_2$ and (*b*) $[Co_2(qpy)_2(O_2CMe)][PF_6]_3$

Table 7 Electrochemical data (V *vs.* ferrocene–ferrocenium) for MeCN solutions of cobalt, nickel and copper complexes. All peak-to-peak separations 70–120 mV

Copper	$Cu^{II}Cu^{II}$–$Cu^{II}Cu^{I}$	$Cu^{II}Cu^{I}$–$Cu^{I}Cu^{I}$					
qpy	+0.15	−0.37					
dpqpy	+0.12	−0.43					
btqpy	+0.148	−0.40					
bcpqpy	+0.18	−0.41					
bdmpqpy	+0.18	*					
bmtqpy	+0.12	−0.43					
Nickel							
qpy				−1.23	−1.81	−1.94	
dpqpy				−1.18	−1.71	−1.90	
btqpy				−1.22	−1.70	−1.90	
bcpqpy				−1.19	−1.66	−1.88	−2.17
bdmpqpy				−1.31	−1.83	−2.04	
bmtqpy				−1.25	−1.79	−1.95	−2.22
Cobalt							
qpy			−1.10	−1.19/−1.37	−1.71	−1.93	−2.11
dpqpy			−1.0		−1.60		
btqpy			−1.0		−1.69	−1.84	
bcpqpy			−0.89	−1.29	−1.6	−1.89	−2.0
bdmpqpy			−1.09	−1.24	−1.54	−1.78	
bmtqpy			−1.02		−1.68		−2.13

* No metal-centred redox process observed.

Table 8 Proton NMR data (δ) for CD_3CN solutions of nickel complexes

	T										B							X							
Ligand					4′		*o*	*p*	*m*	O_2CMe							4‴					*o*	*p*	*m*	Substituent
terpy	135	75	71	44	19	14	—	—	—																
pterpy	134	75	68	44	—	14	11	10	7																
hpterpy	134	76	68	44	—	14	11	—	7																8
bbpbz										47	165	60	49	46	44	17	10								
bmtbpbz										45	160	61	49	43	42	18	—								
qpy	140	75	68	44	18	14				48	158	59	53	46	44	16	15	65	59	42	8	—	—	—	—
dpqpy	140	76	65	45	—	14	18	11	7	47	160	60	51	46	45	15	—	62	60	42	8	8	9	7	—
btqpy	140	75	66	44	—	14	11	—	7	47	160	60	51	46	44	16	—	63	60	41	8	10	—	7	3.3
bcpqpy	142	76	66	45	—	14	11	—	7	50	160	60	51	46	45	15	—	62	60	41	8	10	—	7	—
bhpqpy	140	75	66	45	—	13	11	—	7	49	*	60	54	48	45	16	—	62	59	43	8	10	—	7	3.3
bdmpqpy	140	75	67	46	—	14	11	—	7	48	161	61	53	47	45	15	—	63	60	41	9	10	—	7	4.4
bmtqpy	140	75	65	44	—	13	—	—	—	48	160	59	50	46	44	15	—	62	59	39	8	10	—	7	3.2

* Peak too broad to be observed.

Table 9 Proton NMR data (δ) for CD_3CN solutions of cobalt complexes

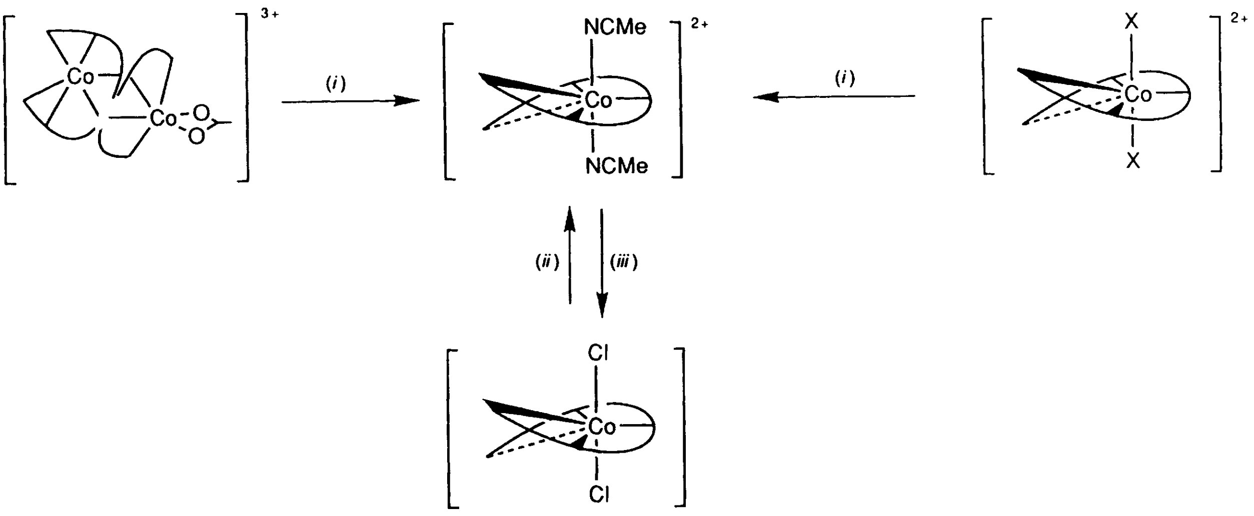
Ligand	$6/6'''$								*o*/*m*	*m*/*o*	Substituent
qpy[a]	134	82	76	75	69	51	22	19			
dpqpy[b]	134	82	76	74	70	51	21	19	13	9	
btqpy	132	81	76	74	70	50	21	19	14	9	
bcpqpy	134	82	75	73	70	50	21	19	14	9	
bhpqpy	133	81	76	74	69	50	21	19	14	8	
bdmpqpy	133	82	77	75	70	50	21	19	14	8	4
bmtqpy	132	81	74	72	69	49	21	19			5

[a] δ 20 for $H^{4',4'''}$. [b] δ 10 for H^{p}.

bipyramidal rather than octahedral, and has no strong ligand field-dictated preference for the cobalt(III) state.

In summary, although qpy forms a double-helical 2:2 complex with cobalt(II), $[Co_2(qpy)_2(O_2CMe)]^{3+}$, substituted derivatives show somewhat different behaviour. The complex with bcpqpy shows a mononuclear single-helical structure in the solid state. The NMR and electrochemical studies reveal that all the complexes give rise to similar mononuclear solution species. This interconversion of single- and double-helical complexes has allowed us to prepare heterobinuclear double-helical complexes by a consideration of the preferred co-ordination environments of particular metal ions.[22]

In conclusion we have demonstrated that cobalt(II) complexes with qpy ligands may show an interconversion between single- and double-helical structures upon dissolution. The solid-state structures of the cobalt(II) complexes are sensitive to the nature of substituents upon the ligand and both mono- and bi-nuclear solid-state complexes may be isolated. No such ligand dependence is observed in the case of copper and nickel(II) complexes of substituted qpy ligands.



Scheme 2 (*i*) MeCN; (*ii*) MeCN, Tl^+; (*iii*) Cl^-

Acknowledgements

We thank the SERC for support (to D. A. T. and E. C. C.) and the award of studentships (to J. V. W.), the Royal Society and Isaac Newton Trust for grants enabling the purchase of spectrometers.

References

1 See, for example, F. Vögtle, *Supramolecular Chemistry*, Wiley, Chichester, 1991; A. F. Williams, C. Floriani and A. E. Merbach, *Perspectives in Coordination Chemistry*, VHCA and VCH, Basel and Weinheim, 1992.

2 C. Dietrich-Buchecker and J.-P. Sauvage, *New J. Chem.*, 1992, **16**, 277; J.-P. Sauvage, *Acc. Chem. Res.*, 1990, **23**, 319.

3 E. C. Constable, *Tetrahedron*, 1992, **48**, 10013.

4 E. C. Constable, J. V. Walker and D. A. Tocher, *J. Chem. Soc., Chem. Commun.*, 1992, 768.

5 F. Krohnke, *Synthesis*, 1976, 1.

6 E. C. Constable, J. Lewis and M. Schröder, *Polyhedron*, 1982, **1**, 311.

7 K. T. Potts, *Bull. Soc. Chim. Belg.*, 1990, **99**, 741 and refs. therein; K. T. Potts, M. J. Cipullo, P. Ralli and G. Theodoris, *J. Org. Chem.*, 1982, **47**, 3027; K. T. Potts, D. A. Usifer, A. Guadalupe and H. D. Abruna, *J. Am. Chem. Soc.*, 1987, **109**, 3961.

8 G. M. Sheldrick, SHELXTL-PLUS, University of Göttingen, 1986.

9 G. M. Sheldrick, SHELX 76, program for crystal structure determination, University of Cambridge, 1976.

10 T. J. Batterham, *N.M.R. Spectra of Simple Heterocycles*, Wiley, New York, 1973.

11 E. C. Constable, A. M. W. Cargill Thompson, D. A. Tocher and M. A. M. Daniels, 1992, **16**, 855 and refs. therein.

12 E. C. Constable, S. M. Elder, J. Healy and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1990, 1669.

13 E. C. Constable, M. G. B. Drew and M. D. Ward, *J. Chem. Soc., Chem. Commun.*, 1987, 1600; M. Barley, E. C. Constable, S. A. Corr, R. C. S. McQueen, J. C. Nutkins, M. D. Ward and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1988, 2655.

14 E. C. Constable, M. D. Ward, M. G. B. Drew and G. A. Forsyth, *Polyhedron*, 1989, **8**, 2551.

15 D. F. Evans, *J. Chem. Soc.*, 1959, 2003.

16 D. R. Eaton and W. D. Phillips in *Advances in Nuclear Magnetic Resonance*, ed. J. S. Waugh, Academic Press, New York, 1965, p. 103; J. Happe and R. L. Ward, *J. Chem. Phys.*, 1963, **39**, 1211; R. J. Fitzgerald and R. S. Drago, *J. Am. Chem. Soc.*, 1968, **90**, 2523.

17 E. C. Constable, J. Lewis, M. C. Liptrot and P. R. Raithby, *Inorg. Chim. Acta*, 1990, **178**, 47.

18 E. C. Constable, J. V. Walker and E. M. Hutchinson, unpublished work.

19 E. C. Constable, M. J. Hannon and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1993, 1883.

20 K. A. Gheysen, K. T. Potts, H. C. Hurrell and H. D. Abruna, *Inorg. Chem.*, 1990, **29**, 1589.

21 E. C. Constable, S. M. Elder, P. R. Raithby and M. D. Ward, *Polyhedron*, 1991, **10**, 1395.

22 E. C. Constable and J. V. Walker, *J. Chem. Soc., Chem. Commun.*, 1992, 884.

Received 25*th January* 1993; *Paper* 3/00453H