# Interconversion and Ligand Dependence in Mononuclear and Dinuclear Cobalt(II) Helicate Complexes of 2,2′ : 6′,2″ : 6″,2‴ : 6‴,2⁗-Quinquepyridines; Crystal and Molecular Structure of Aqua(methanol)[4′,4‴-bis(4-chlorophenyl)-2,2′ : 6′,2″ : 6″,2‴ : 6‴,2⁗-quinquepyridine]cobalt(II) Bis(hexafluorophosphate)

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The crystal and molecular structure of $[Co(cp_2qpy)(MeOH)(H_2O)][PF_6]_2$ ($cp_2qpy$ = 4′,4‴-bis(4-chlorophenyl)-2,2′ : 6′,2″ : 6″,2‴ : 6‴,2⁗-quinquepyridine reveal the cation to be a mono-helical seven-coordinate species [$P2_1/a$, $a$ = 17.441(4), $b$ = 11.765(4), $c$ = 20.402(6) Å, $\beta$ = 105.24(2)°] unlike 2,2′ : 6′,2″ : 6″,2‴ : 6‴,2‴ quinquepyridine (qpy), which forms a double-helical 2 : 2 complex with cobalt(II), $[Co_2(qpy)_2(OAc)]^{3+}$; in acetonitrile solution the qpy and $cp_2qpy$ complexes give rise to common mononuclear species.

There is considerable current interest in molecular topology, with particular emphasis being placed on the ability of metal ions to control the configuration of an organic ligand.[1] Double- and triple-helical coordination compounds are both aesthetically satisfying and synthetically challenging, and embody the control features needed for the assembly of larger and more complex ligand arrays.[2] We have shown that the higher oligopyridines are of particular interest in this respect.[3–5] In this paper we describe our investigations of some anomalies associated with cobalt(II) complexes of

2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridines, and report the observation of novel interconversions of mono- and di-nuclear helicates. We have previously shown that the reaction of 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine (qpy) with cobalt(II) acetate leads to the formation of the compound $[Co_2(qpy)_2\text{-}(OAc)][PF_6]_3$,[4,5] which contains a dinuclear double-helical cation in the solid state.[5] The electrochemical properties of this compound were complicated and time-dependent. In contrast to these observations, the reaction of 4′,4‴-bis(methylthio)-2,2′ : 6′,2″ : 6″,2‴ : 6‴,2⁗-quinquepyridine ($ms_2qpy$) with cobalt(II) chloride yields the mononuclear seven-coordinate complex $[Co(ms_2qpy)Cl_2]$.[6] We now describe a systematic study of the behaviour of cobalt(II) with 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridines.

Upon heating suspensions of 4′,4‴-diphenyl-2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine ($Ph_2qpy$), 4′,4‴-bis-(4-methylphenyl)-2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine ($Tol_2qpy$) or 4′,4‴-bis(4-chlorophenyl)-2,2′:6′,2″:6″,2‴ : 6‴,2⁗-quinquepyridine ($cp_2qpy$) in methanol with cobalt(II) acetate, the ligands dissolved to give orange-brown solutions of cobalt(II) complexes.† Treatment with $[NH_4][PF_6]$ resulted in the precipitation of pale orange solids, which were recrystallised from MeCN/diethyl ether or methanol to yield good quality crystals. The FAB mass spectra (3-nitrobenzyl alcohol matrix) of all of the products exhibit peaks assigned to $[CoL(PF_6)]$ (L = $Ph_2qpy$, *m/z* 743; L = $Tol_2qpy$, *m/z* 771; L = $cp_2qpy$, *m/z* 811), but only the complex with $Tol_2qpy$ exhibited any peaks assigned to dinuclear species, and these were of very low intensity. This is in contrast to the complex with qpy, which exhibits high intensity peaks assigned to dinuclear species. The complexes are paramagnetic, but we have been unable to obtain well-resolved EPR spectra.

The complexes all dissolve in MeCN to give yellow solutions. In MeCN solution ($[Bu^n_4N][BF_4]$ supporting electrolyte, double Pt bead working/auxiliary electrodes, Ag/AgCl reference, internal Fc/Fc$^+$ standard) solutions of each complex are electrochemically active. None of the complexes show any oxidation waves corresponding to a Co$^{II}$/Co$^{III}$ couple, but each gives a pseudoreversible reduction wave close to −1.0 V (L = qpy, −1.10 V; L = $Ph_2qpy$, −1.0 V; L = $Tol_2qpy$, −1.0 V; L = $cp_2qpy$, −0.89 V; all *vs.* Fc/Fc$^+$). Each complex also shows a series of further reduction waves to more negative potentials. These results suggest that similar solution species are obtained in *all* cases. In order to further elucidate the structures of these complexes, we have determined the crystal and molecular structure of a cobalt(II) complex of one of the substituted ligands.‡

Slow cooling of the solution obtained from the reaction of $cp_2qpy$ with cobalt(II) acetate in methanol after the addition of $[NH_4][PF_6]$ gave good quality, red crystals of a complex $[Co(cp_2qpy)(MeOH)(H_2O)][PF_6]_2$; the crystal and molecular structure of one of the two enantiomers of this cation present in the unit cell is presented in Fig. 1(*a*), together with a space filling representation in Fig. 1(*b*). The cation is mononuclear, with the $cp_2qpy$ acting as a pentadentate ligand and forming 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 $cp_2qpy$ ligand minimises the interactions that 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 atom they contain). The chlorophenyl substituents are not coplanar with the pyridine rings to which they are attached, but are skewed (2/Ar, 26.4°; 4/Ar, 18.8°). These are similar to the pyridine/aryl twistings which we have previously observed in the complex $[Ni(Phtpy)_2]Cl_2$ (Phtpy = 4′-phenyl-terpyridine).[7] The $PF_6$ counter-anions do not 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 [Co(1)–N(1), 2.283(8) Å; Co(1)–N(5), 2.247(9) Å] are significantly longer than those to the 'inner' rings [Co(1)–N(2), 2.180(8) Å; Co(1)–N(3), 2.229(9) Å; Co(1)–N(4), 2.179(8) Å]. In view of the similarities in the solution properties of cobalt(II) complexes of qpy and $cp_2qpy$ and their differing solid-state structures we have further investigated these complexes.

Solutions of the solid-state double-helical complex $[Co(qpy)_2(OAc)][PF_6]_3$ and the solid-state mono-helical complex

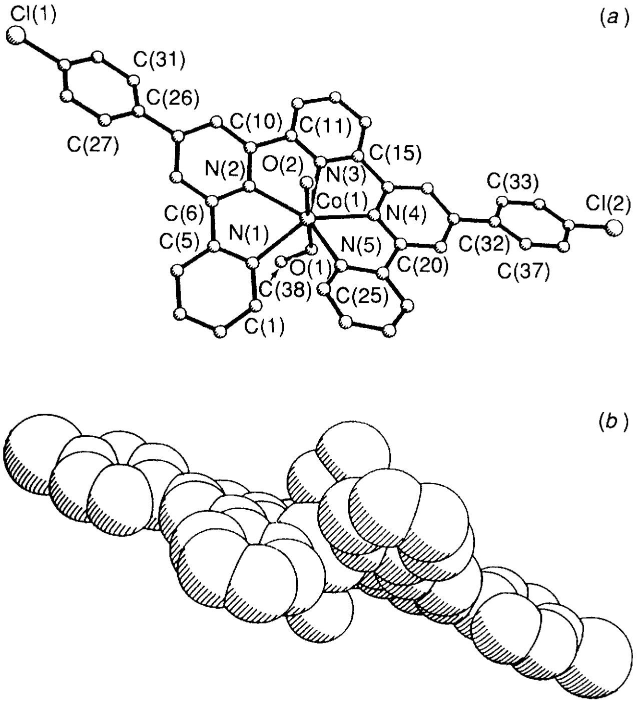

**Fig. 1** (*a*) The crystal and molecular structure of $[Co(cp_2qpy)(MeOH)(H_2O)][PF_6]_2$ showing the numbering scheme adopted Co(1)–N(1) 2.283(8), Co(1)–N(2) 2.180(8), Co(1)–N(3) 2.229(9), Co(1)–N(4) 2.179(8), Co(1)–N(5) 2.247(9), Co(1)–O(1) 2.209(9), Co(1)–O(2) 2.183(8) Å; N(1)–Co(1)–N(2) 71.2(3), N(1)–Co(1)–N(3) 138.4(3), N(2)–Co(1)–N(3) 70.7(3), N(1)–Co(1)–N(4) 143.8(3), N(2)–Co(1)–N(4) 142.1(3), N(3)–Co(1)–N(4) 71.4(3), N(1)–Co(1)–N(5) 82.2(3), N(2)–Co(1)–N(5) 144.4(3), N(3)–Co(1)–N(5) 139.4(3), N(4)–Co(1)–N(5) 71.4(3), N(1)–Co(1)–O(1) 80.8(3), N(2)–Co(1)–O(1) 98.4(3), N(3)–Co(1)–O(1) 88.7(3), N(4)–Co(1)–O(1) 80.0(3), N(5)–Co(1)–O(1) 100.2(3), N(1)–Co(1)–O(2) 103.1(3), N(2)–Co(1)–O(2) 182.6(3), N(3)–Co(1)–O(2) 88.0(3), N(4)–Co(1)–O(2) 96.9(3), N(5)–Co(1)–O(2) 81.0(3) and (*b*) a space-filling representation of the cation.

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† All new ligands gave satisfactory microanalysis results and $^1$H NMR and mass spectra.

‡ *Crystal data*: $C_{38}H_{29}N_5O_2Cl_2P_2F_{12}Co$, orange plates, $M$ = 936.54, monoclinic, space group $P2_1/a$, $a$ = 17.441(4), $b$ = 11.765(4), $c$ = 20.402(6) Å, β = 105.24(2)°, $U$ = 4039 Å$^3$, $Z$ = 4, $D_c$ = 1.66 g cm$^{-3}$, Mo-Kα radiation (λ = 0.71073 Å), μ(Mo-Kα) = 7.30 cm$^{-1}$. 6036 Reflections collected on a four circle diffractometer with 2θ(max.) 50°. The data were averaged and 3346 unique data with $I \geqslant 3.0\sigma(I)$ were used in structure solution and refinement. The structure was solved by Patterson methods followed by iterative least-squares refinement and difference Fourier synthesis and refined (Co, Cl, P, F, O, N, C anisotropic) to $R = 0.0851$, $R_w = 0.0766$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

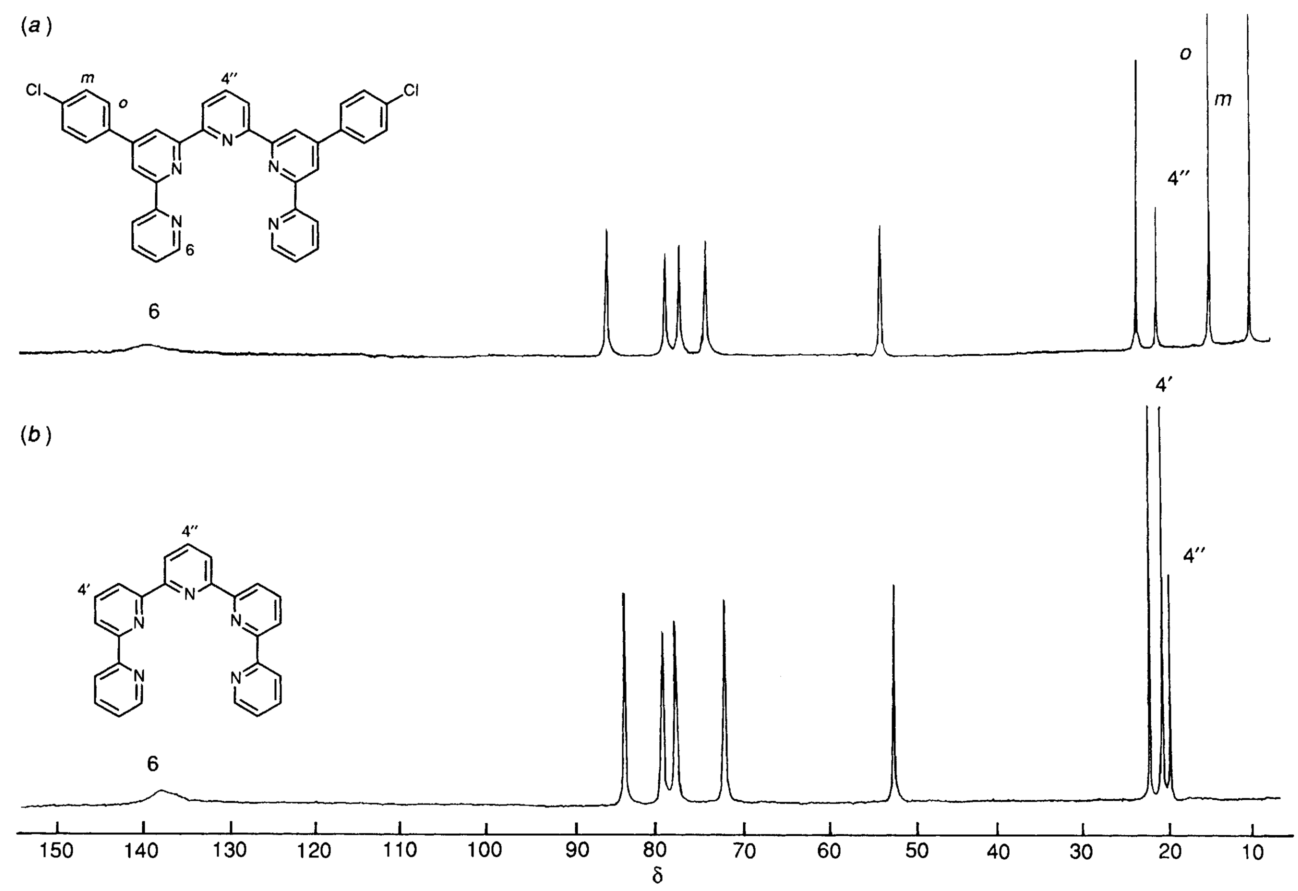

**Fig. 2** $^1H$ NMR spectra of $CD_3CN$ solutions of (*a*) $[Co_2(qpy)_2\text{-}(OAc)][PF_6]_2$ and (*b*) $[Co(cp_2qpy)(MeOH)(H_2O)][PF_6]_2$ with partial assignments

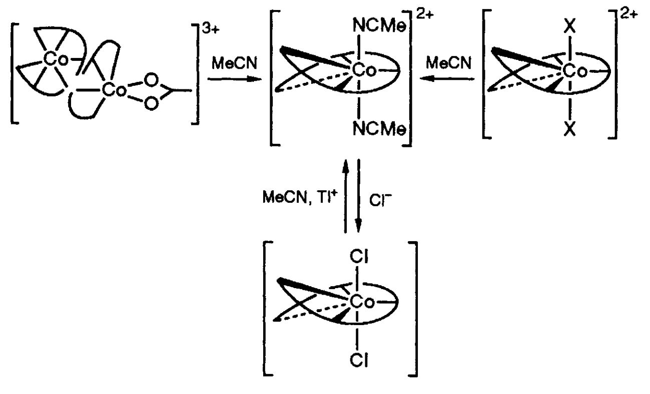

**Fig. 3** Interconversion of double-helical and monohelical cobalt(II) complexes with qpy ligands

$[Co(cp_2qpy)(MeOH)(H_2O)][PF_6]_2$ in $CD_3CN$ exhibit very similar, well-resolved paramagnetically shifted $^1H$ NMR spectra (Fig. 2). The only detectable differences in the spectra result from the replacment of the $H_{4',4'''}$ protons by aryl groups on passing from the qpy to the $cp_2qpy$ complex. In each case, the number of resonances in the spectrum indicates that the ligand is symmetrical about the central pyridine ring on the NMR time-scale; the qpy complex exhibits nine resonances and the $cp_2qpy$ complex ten. This is only compatible with the solution species possessing the mono-helical structure, presumably with axial acetonitrile ligands (Fig. 3). The lowest field resonances (δ 134–135) are assigned to $H_6$; attempts to assign the remainder of the spectrum by COSY or single-frequency decoupling experiments were unsuccessful. A resonance at δ ≈ 19.0 may be reliably assigned to $H_{4''}$ as it is of half the intensity of the others. Similarly, 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 spectra of the substituted compounds. The resonances of the aromatic substituents may be reliably assigned by a 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). The observation of a common mono-helical solution species explains the complex electrochemical behaviour, and the formation of such a seven-coordinate species also suggests reasons for the difficulty in oxidation to cobalt(III) complexes. This also provides an explanation for our inability to resolve the double-helical $[Co_2(qpy)_2(OAc)]^{3+}$ cation! A combination of ESR and NMR spectroscopy, mass spectrometry and solid-state structural studies allow us to probe such interconversions in other metal complexes of qpy and its derivatives: dinickel and dicopper complexes maintain the double-helical structure in solution, whereas cobalt and iron complexes give rise to mono-helical solution species and varying solid-state structures.§

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§ Details of studies on other metal complexes will be reported in full at a later date.

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