The Systematic Synthesis of Heterobimetallic Double-helical Complexes of 2,2′ : 6′,2″ : 6″,2‴ : 6‴,2⁗-Quinquepyridines

Edwin C. Constable* and Juliet V. Walker

Cambridge Centre for Molecular Recognition, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK

2,2′ : 6′,2″ : 6″,2‴ : 6‴,2⁗-Quinquepyridine ligands (L) form double-helical 2 : 2 or mono-helical 1 : 1 complexes with transition metals; solutions of cobalt(II) complexes contain the monohelical seven-coordinate cation $[CoL(\mathbf{S})_2]^{2+}$ (**S** = H_2O, MeOH or MeCN) which reacts with silver(I) or copper(I) to give the heterobinuclear double-helical complexes $[CoML_2]^{3+}$.

We and others are currently interested in the ability of metal ions to control the configurations of organic ligands and in the use of metal ions to direct molecular topology.[1] Double- and triple-helical coordination compounds may be prepared, and are both aesthetically satisfying and synthetically challenging, and allow us to develop an understanding of 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] and have recently described some novel interconversions of mononuclear and

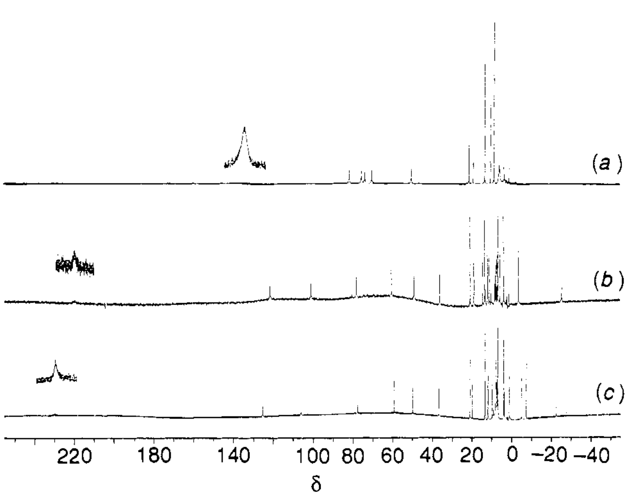
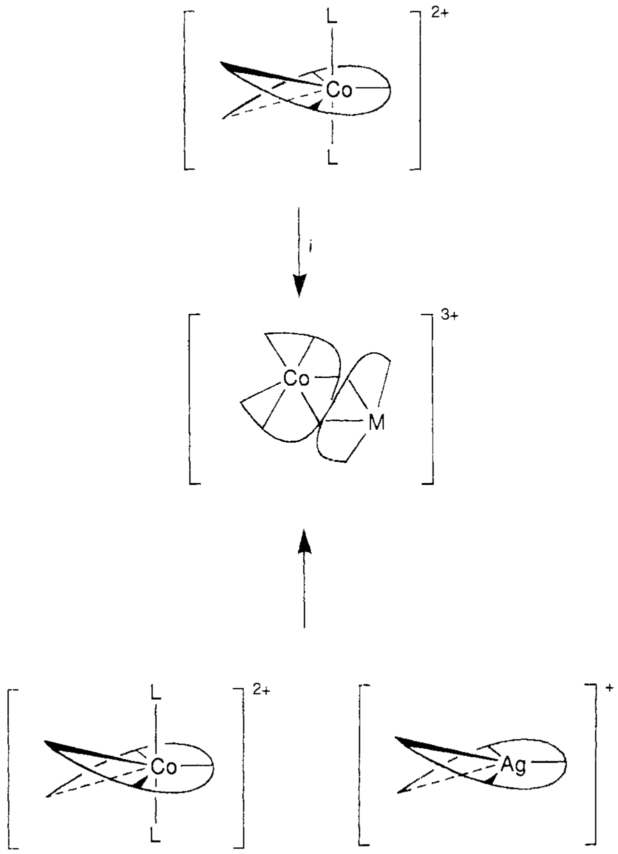


Fig. 1 ^{1}H NMR spectra of CD$_3$CN solutions of (*a*) [Co(Ph$_2$qpy)(MeCN)$_2$]$^{2+}$, (*b*) [CoAg(Ph$_2$qpy)$_2$]$^{3+}$ and (*c*) [CoCu(Ph$_2$qpy)$_2$]$^{3+}$



Scheme 1 Interconversion of double-helical and monohelical cobalt(II) complexes with qpy ligands: i, M$^+$, M = Ag, Cu

binuclear cobalt(II) helicates.[4] To date, no examples of heteropolynuclear multiple-helical complexes have been described, and attempts to prepare such complexes by statistical methods have been unsuccessful. We now describe the utilisation of mono-helical mononuclear cobalt(II) complexes for the non-statistical synthesis of heterobinuclear cobalt(II)–copper(I) and cobalt(II)–silver(I) double-helicates.

In the solid state, 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine (qpy) forms a double-helical dicobalt(II) cation, [Co$_2$(qpy)$_2$(OAc)]$^{3+}$, whereas 4′,4‴-diphenyl-2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine (Ph$_2$qpy) or 4′,4‴-bis(4-chlorophenyl)-2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine (cp$_2$qpy) form the mono-helical seven-coordinate species [Co(Ar$_2$qpy)(S)$_2$]$^{2+}$ (Ar$_2$qpy = Ph$_2$qpy or cp$_2$qpy; S = MeCN, H$_2$O or MeOH).[4] Solutions of any of the above complexes in MeCN, EtOH or MeOH contain the mono-helical cations [Co(L)(S)$_2$]$^{2+}$ (L = qpy, Ph$_2$qpy or cp$_2$qpy; S = MeCN, EtOH or MeOH).[4] In the past, we have rationalised the formation of double-helical complexes in terms of metal–ligand recognition events in which the acceptor properties of the metal ion were matched up to the donor properties of the ligands. Specifically, the ten donor atoms of a double-helical array of two qpy ligands can accommodate a six-coordinate *pseudo*octahedral and a four-coordinate *pseudo*tetrahedral metal centre. We considered that the facile interconversion of the double- and mono-helical cobalt(II) complexes would allow us to convert a mono-helical cobalt(II) complex to a heterobimetallic double-helical complex upon reaction with a metal centre such as copper(I) or silver(I); this would place the cobalt(II) in a *pseudo*octahedral site and the silver(I) or copper(I) in a *pseudo*tetrahedral site.

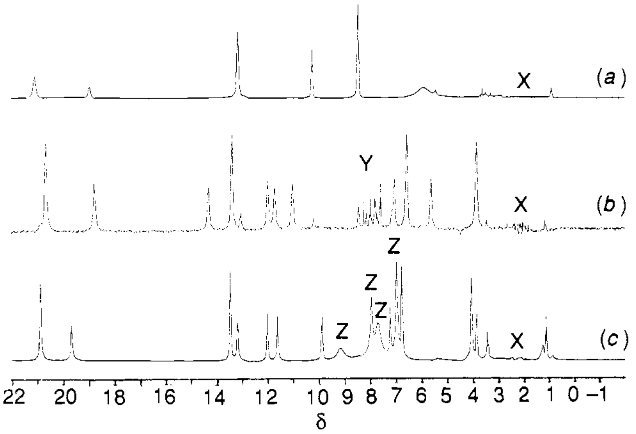


Fig. 2 Expansion of the δ −1 to +22 region of the ^{1}H NMR spectra of CD$_3$CN solutions of (*a*) [Co(Ph$_2$qpy)(MeCN)$_2$]$^{2+}$, (*b*) [CoAg(Ph$_2$qpy)$_2$]$^{3+}$ and (*c*) [CoCu(Ph$_2$qpy)$_2$]$^{3+}$. Peaks marked X are residual solvent resonances following background subtraction; peaks marked Y and Z are due to trace amounts of mononuclear [AgL]$^+$ and binuclear [Cu$_2$L$_2$]$^{3+}$ species.

Treatment of acetonitrile solutions containing [Co(L)(MeCN)$_2$]$^{2+}$ (L = qpy, Ph$_2$qpy or cp$_2$qpy) with an excess of silver(I) acetate resulted in no colour changes and no changes in the paramagnetically shifted ^{1}H NMR spectrum of the cation [Fig. 1(*a*)]. In contrast, colour changes were observed upon the reaction of solutions of [Co(L)(S)$_2$]$^{2+}$ in methanol or ethanol with [Cu(MeCN)$_4$]$^+$ or Ag$^+$. Treatment of the solutions obtained from the reaction of one equivalent of cobalt complex with half an equivalent of silver(I) or copper(I) with [NH$_4$][PF$_6$] or Na[BF$_4$] resulted in the precipitation of yellow or brown solids respectively. The FAB mass spectra (3-nitrobenzyl alcohol matrix) of the products exhibit peaks assigned to {CoML$_2$X$_n$} (M = Ag or Cu; L = qpy, Ph$_2$qpy or cp$_2$qpy; X = BF$_4$ or PF$_6$).† Although the complexes may be obtained analytically pure by recrystallisation from acetonitrile by the diffusion of diethyl ether vapour into the solutions, repeated attempts to obtain X-ray quality crystals of any of the complexes have been unsuccessful. The cobalt(II)–silver(I) complexes may also be cleanly obtained in quantitative yield

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† [CoCu(cp$_2$qpy)$_2$][BF$_4$]$_2$, *m/z* 1515 {CoCu(cp$_2$qpy)$_2$(BF$_4$)$_2$}, 1427 {CoCu(cp$_2$qpy)$_2$(BF$_4$)}; [CoCu(Ph$_2$qpy)$_2$][PF$_6$]$_2$, *m/z* 1491 {CoCu(Ph$_2$qpy)$_2$(PF$_6$)$_2$}, 1347 {CoCu(Ph$_2$qpy)$_2$(PF$_6$)}, 1201 {CoCu(Ph$_2$qpy)$_2$}; [CoAg(Ph$_2$qpy)$_2$][PF$_6$]$_2$, *m/z* 1537, {CoAg(Ph$_2$qpy)$_2$(PF$_6$)$_2$}, 1391 {CoAg(Ph$_2$qpy)$_2$(PF$_6$)}; [CoCu(qpy)$_2$][PF$_6$]$_2$, *m/z* 1190 {CoCu(qpy)$_2$(PF$_6$)$_2$}, 1045 {CoCu(qpy)$_2$(PF$_6$)}; [CoAg(qpy)$_2$][PF$_6$], *m/z* 1230 {CoAg(qpy)$_2$(PF$_6$)$_2$}, 1085 {CoAg(qpy)$_2$(PF$_6$)}; all with appropriate isotopomer distributions.

Table 1 ^{1}H NMR spectra (δ values)

	$[CoM(Ph_2qpy)_2]^{3+}$		$[CoM(qpy)_2]^{3+}$	
	M = Cu	M = Ag	M = Cu	M = Ag
	229	221	231	220
	125.1	122.1	123	121
	105.9	101.5	105	97.7
	77.4	78.3	77.0	78.9
	59.0	60.6	58.0	61.7
	49.7	49.2	51.2	50.5
	36.6	36.1	38.1	38.5
	19.7	18.9	19.8	18.2
	13.2	14.4	12.3	13.7
	11.6	11.7	11.0	10.8
	9.9	11.0	10.0	10.79
	3.8	5.6	4.0	5.6
	−4.9	−3.7	−5.0	−2.8
	−7.4	−3.8	−6.5	−3.6
	−22.6	−25.6	−22.0	−17.4
$Ph_{o/m}$	20.9	20.7		
$Ph_{o/m}$	13.5	13.4		
$Ph_{o/m}$	6.7	6.6		
$Ph_{o/m}$	4.0	3.8		
Ph_p	12.0	12.0		
Ph_p	7.2	7.0		
H-4′			26.2	25.5
H-4′			12.29	3.5

by the reaction of solutions of the monohelical cations $[Co(L)(\mathbf{S})_2]^{2+}$ with the monohelical[5] silver cations $[AgL]^+$ (Scheme 1).

These new complexes all dissolve in MeCN to give yellow (Ag) or brown (Cu) solutions. MeCN solutions of each complex are electrochemically active (cyclic voltammetry, $[Bu^n{}_4N][BF_4]$ supporting electrolyte, double Pt bead working/auxiliary electrodes, internal Fc/Fc^+ standard). The cobalt(II)–copper(I) complexes exhibit reversible copper(II)/copper(I) processes at modest potentials (L = Ph_2qpy, $E_{1/2}$ = 0.112 V *vs.* Fc/Fc^+), and a reversible cobalt(III)/cobalt(II) couple at +0.61 V *vs.* Fc/Fc^+. The only oxidation process observed in the cobalt(II)–silver(I) complexes is a reversible cobalt(III)/cobalt(II) process at 0.40 V *vs.* Fc/Fc^+. With each complex, there are several ligand-based reductions, often obscured by irreversible absorption phenomena. The observation of the cobalt(II)/cobalt(III) couples is in contrast to the behaviour of solutions of the homonuclear cobalt(II) complexes {which contain the seven-coordinate $[CoL(\mathbf{S})_2]^{2+}$ species} which do not exhibit any such processes; this is indirect evidence for the cobalt occuping a six-coordinate site with the strong-field oligopyridine ligands stabilising cobalt(III).

Solutions of the new cobalt(II)–silver(I) and cobalt(II)–copper(I) complexes in CD_3CN exhibit well-resolved paramagnetically shifted ^{1}H NMR spectra [Fig. 1(*b*) and (*c*)] which differ from those of the mononuclear cobalt(II) solution species [Fig. 1(*a*)] and also from those of the homonuclear silver and copper complexes. The total number of resonances in the spectrum indicates that each ligand is asymmetrical on the NMR time-scale, with each proton being in a chemically and magnetically different environment; the Ph_2qpy complex exhibits 21 resonances and the qpy complex 17 (Table 1). This is compatible with the solution species possessing the heterobinuclear double-helical structure (Scheme 1). Attempts to assign the spectra fully have been unsuccessful, with the lines being too broad for one- or two-dimensional decoupling techniques to be applied. Partial assignments made on the basis of the differences between the complexes with the three ligands are indicated in Table 1 and in Figs. 1 and 2.

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