Heterodimetallic double helicates from redistribution reactions

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Dinickel(II) and dicopper(I) double helicates of 4′,4‴-bis(methylsulfanyl)-2,2′:6′,2″:6″,2‴:6‴,2‴′-quinquepyridine (ms2qpy) ligands react to form heterodimetallic double helicates [CuNi(ms2qpy)2]3+; the complex [CuNi(ms2-qpy)2][PF6]3·4H2O is structurally characterised.

Oligopyridines and complexes containing oligopyridine metal-binding domains are versatile motifs in metallosupramolecular chemistry.[1,2] Multiple helical complexes have been shown to result from the interaction of such ligands with appropriate metal centres.[3] In order to probe the subtleties of this self-assembly process we have addressed questions of directionality[4] and metal-ion selectivity[5] in helicate assembly with oligopyridines. Heterodimetallic double helicates have hitherto been prepared either from heterotopic ligands[6] or by the reaction of two monohelical species.[5] Here, we describe the synthesis of heterodinuclear double helicates by the ligand-field dictated redistribution of two preformed homometallic double helicates.

Copper(I) forms both 2:2 and 3:2 double helicates with qpy ligands[1,7] although the 2:2 complex is the dominant solution species at 1:1 metal:ligand stoichiometries. Of the ten donor atoms of the double-helical array of two qpy ligands, only eight are involved in binding the metal ions. In contrast, nickel(II)

forms dinuclear [6 + 4 + 2][1] double-helical solution species containing two octahedral nickel(II) centres;[1,8] the double-helical array of two qpy ligands provides ten of the required donor atoms, with the two additional donors coming from acetate or solvent ligands. As oligopyridines are relatively strong-field ligands we argued that the nickel in the N4O2 environment was destabilised on ligand-field grounds with respect to the N6 environment and furthermore that the coordination of all of the potential donor atoms within the qpy ligands should be thermodynamically favourable. Accordingly, we considered the possibility of a redistribution reaction between [Cu2(ms2qpy)2]2+ ([4 + 4]) and [Ni2(ms2qpy)2-(O2CMe)]3+ ([6 + 4 + 2]) to yield [CuNi(ms2qpy)2]3+ ([6 + 4]) with the nickel in the six-coordinate and the copper in the four-coordinate site (Scheme 1).

The addition of a red solution of [Cu2(ms2qpy)2]2+ to a green solution of [Ni2(ms2qpy)2(O2CMe)]3+ gave a red solution from which a red solid was precipitated upon the addition of [NH4][PF6]. Recrystallisation from aqueous acetone yielded red needles of [CuNi(ms2qpy)2][PF6]3 in 61% yield. Microanalysis and fast atom bombardment mass spectrometry confirmed the formulation [m/z 1370, 1372 {CuNi(ms2qpy)2(PF6)2} and 1225, 1227 {CuNi(ms2qpy)2(PF6)}]. The 1H NMR spectrum of the complex differs considerably from that of [Ni2(ms2qpy)2-(O2CMe)]3+ with fewer paramagnetically shifted resonances and new resonances in the region δ 6–10 assigned to a diamagnetic {Cu(bpy)2} domain.

Recrystallisation from aqueous acetone yielded X-ray quality crystals of the complex [CuNi(ms2qpy)2][PF6]3·4H2O† and the molecular structure of one of the enantiomers of the double-helical cation present in the lattice is shown in Fig. 1. As predicted, the nickel is in the six-coordinate and the copper in the four-coordinate site. The Ni–N distances [2.012(10)–2.221(9) Å] closely resemble those observed for the

SMe   SMe

R = MeS   ms2qpy
R = H   qpy

[Cu2(qpy)2]2+   [Ni2(qpy)2]3+   [CuNi(qpy)2]3+
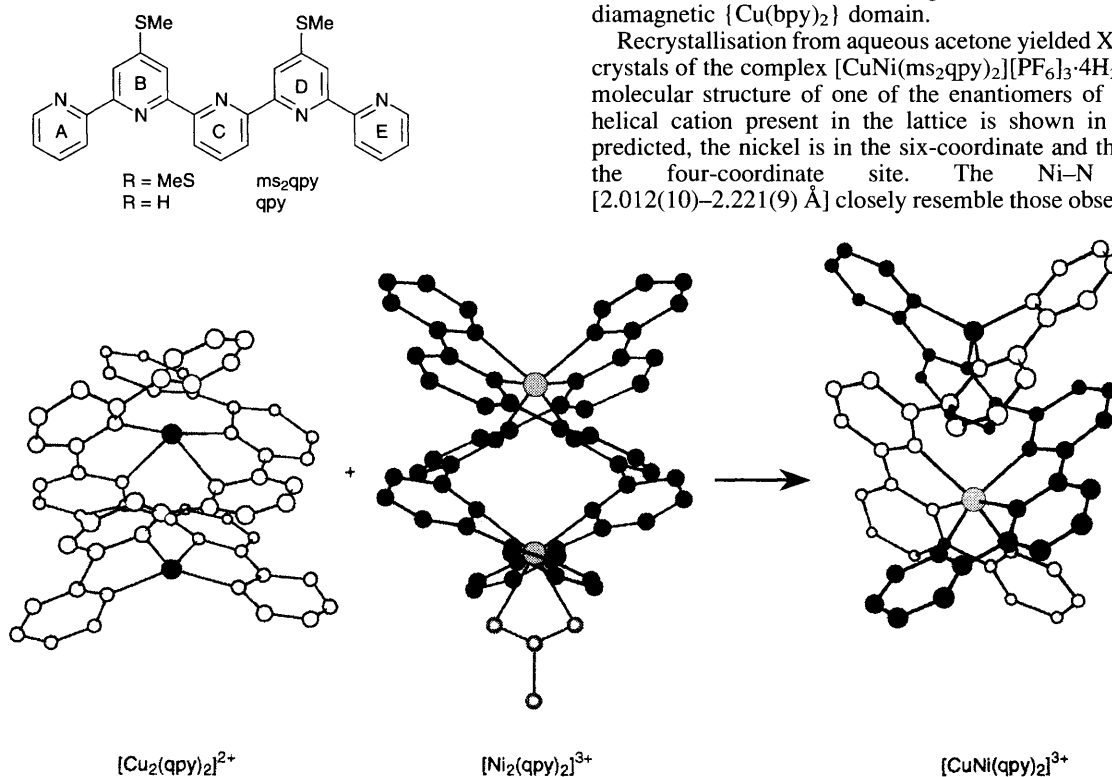
Scheme 1

nickel in the N_6 environment in other double-helical nickel qpy complexes.[8] Similarly, the Cu–N distances [1.997(9), 2.005(10) Å] are similar to those in other structurally characterised copper(I) qtpy complexes.[7] The tpy and bpy domains of each ligand are essentially planar and almost orthogonal with an interplanar angle of 89.6° between them. There are extensive intrastrand stacking interactions between the two ligands in the double-helical cation. The intermetallic distance is 4.70 Å.

In the same way that the previously reported heterodinuclear complex [CoAg(qpy)$_2$][PF$_6$]$_3$ exhibited intercation interactions
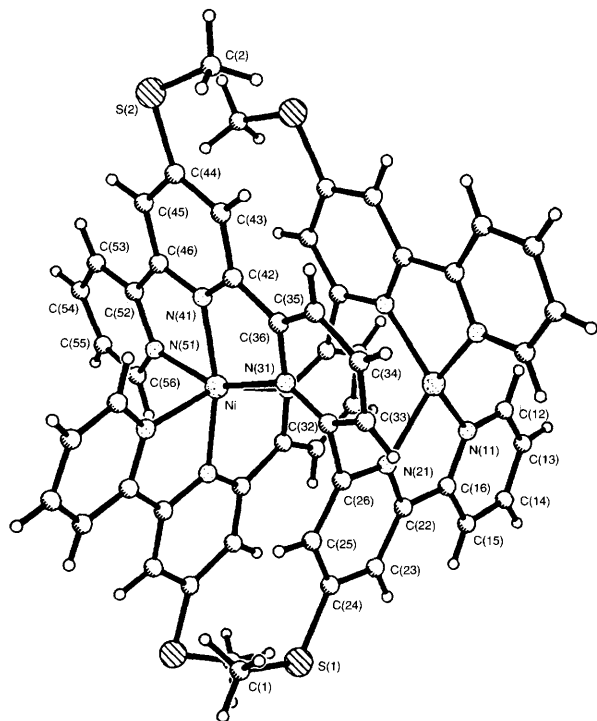

Fig. 1 Crystal and molecular structure of one enantiomer of the cation present in [CuNi(ms2qpy)$_2$][PF$_6$]$_3$·4H$_2$O showing the numbering scheme adopted. Selected bond lengths (Å): Cu–N(11) 1.997(9), Cu–N(21) 2.005(10), Ni–N(31) 2.221(9), Ni–N(41) 2.012(10), Ni(1)–N(51) 2.133(10).
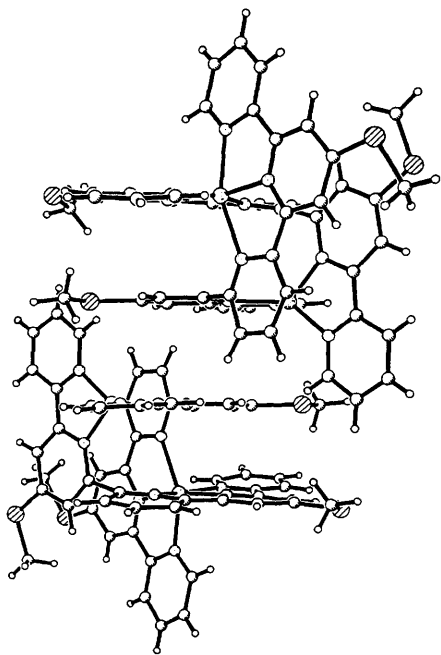

Fig. 2 The packing of the cations in the crystal lattice showing the head-to-head stacking interactions between the copper ends of cations of opposite P or M helical chirality

in the solid state, so are there stacking interactions between adjacent cations wtih this complex. Head-to-head stacking interactions between cations of opposite helical chirality (P and M) lead to 3.93 Å coplanar arrangements of the {Cu(bpy)$_2$} domains of adjacent cations; however, the interactions are between the A ring of one cation and the B ring of the other, resulting in a herring-bone pattern and relatively long Cu···Cu distances of 7.63 Å (Fig. 2).

This coding for helicate formation may be further extended. For example, heterodinuclear silver–nickel complexes result from the reaction of [Ni$_2$(qpy)$_2$(O$_2$CMe)]$^{3+}$ with 2 equiv. of [Ag(qpy)]$^+$. We are currently investigating additional ligand-field imposed control in the assembly of helicates with sequential and non-sequential ligands.

Footnote

† *Crystal data*: red crystal, C$_{54}$H$_{42}$CuF$_{18}$N$_{10}$NiO$_4$P$_3$S$_4$, M = 1580.4, monoclinic, space group $C2/c$, a = 21.873(4), b = 18.560(4), c = 15.061(3) Å, β = 90.65(3)°, U = 6114(2) Å^3, Z = 4, D_c = 1.717 g cm^{-3}, $F(000)$ = 3.184, λ(Mo-Kα) = 0.71073 Å, μ(Mo-Kα) = 0.982 mm^{-1}. Intensity data were collected by the ω-scan method (3.68 < 2θ < 45°); for a crystal of dimensions 0.35 × 0.34 × 0.31 mm maintained at 153(2) K; 3959 (3862 independent) reflections were used in the structure solution. The structure was solved and refined using SHELXL93 to give final $R1$ and $wR2$ values of 0.1015 and 0.2828 [I > 2σ(I)] respectively. The two metal atoms are in special positions and the molecule has crystallographic symmetry. The two ligand strands are, thus, crystallographically equivalent. The relatively high R factors are attributable to disorder of the PF$_6^-$ anions and of the solvent water molecules. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/262.

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