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Self-assembly of an organometallic side-by-side double helix

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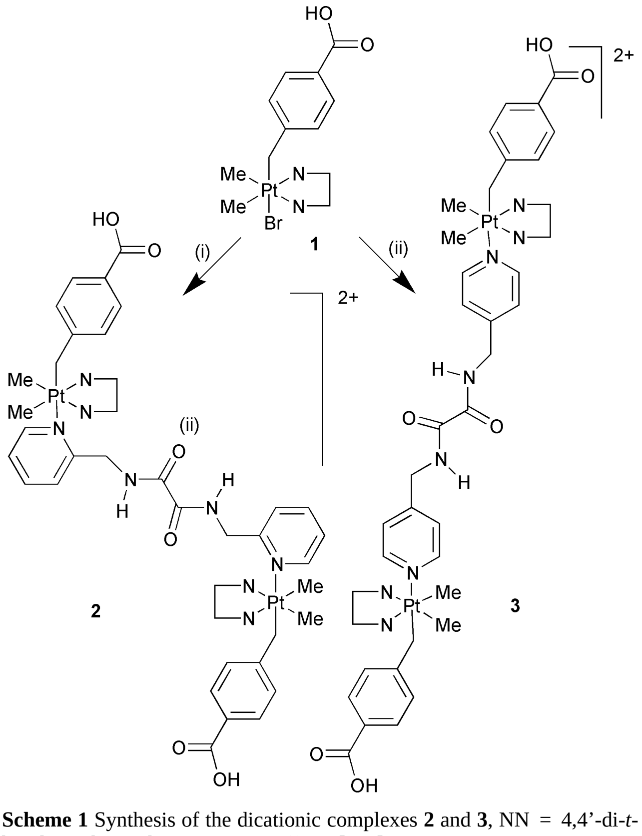
The first polymeric organometallic double helix has been synthesized by self-assembly through hydrogen bonding by using a biomimetic strategy and a new side-by-side structural motif.

There is great interest in the synthesis of helical metal complexes.[1] Most examples of such compounds can be described as either coordination helicates or as organic helices with metals coordinated as side groups, and they are often binuclear or oligonunuclear compounds.[1] However, several elegant examples of helical coordination polymers with metals in the backbone have been obtained by using appropriately designed bridging ligands, with individual building blocks connected by self-assembly through either coordinate bonds, hydrogen bonds or combinations of the two.[1,2] This paper reports what is believed to be the first polymeric organometallic double helix, using hydrogen bonding between amide groups to crosslink the individual helical chains.

The synthesis of the building blocks for self assembly was achieved according to Scheme 1 by coupling two organoplatinum(IV) units, **1**, having carboxylic acid groups appended to one of the alkylplatinum groups, through bridging bis(pyridyl) ligands to give the dicationic complexes **2** and **3** as the hexafluorophosphate salts.† [3,4]



Scheme 1 Synthesis of the dicationic complexes **2** and **3**, NN = 4,4'-di-*t*-butyl-2,2′-bipyridine. *Reagents*: (i) Ag[PF$_6$], 2-pyCH$_2$NHCOCONHCH$_2$-2-py, and (ii) Ag[PF$_6$], 4-pyCH$_2$NHCOCONHCH$_2$-4-py.

The primary self-assembly is expected to occur by hydrogen bonding through the carboxylic acid groups to give a one-dimensional polymer.[3] However, the bis(pyridyl) ligands pyCH$_2$NHCOCONHCH$_2$py, with py = 2-pyridyl in **2** or 4-pyridyl in **3**, contained amide groups in the bridge. These units were expected both to induce helicity and to take part in further self-assembly.

The structure of dicationic complex **2** is shown in Fig. 1. It forms a zigzag one-dimensional polymer by hydrogen bonding between the carboxylic acid groups. There is local helicity in the molecule but there is a centre of symmetry at the midpoint of the dication so the polymer chain is racemic (*PMPM*...) in its overall conformation. The amide groups do not participate in the self-assembly in this case. Each NH group hydrogen bonds weakly to a fluorine atom of a [PF$_6$]$^-$ anion, and each carbonyl group is directed towards a Bu$_2$bipy ligand.

The remarkable structure of complex **3** is shown in Fig. 2. Again, a one dimensional polymer chain is formed by head-to-tail [R$_2^2$(8)] hydrogen bonding between carboxylic acid groups, with distances O(69)$\cdots$O(80A) 2.77 Å and O70$\cdots$O(79A) 2.55 Å. However, there are two important differences from the structure of **2**. First, the flexible ligand *N*,*N*-bis(pyridin-4-ylmethyl)oxalamide in complex **3** induces formation of long range helicity.[5] The twists at the two CCH$_2$N and CCH$_2$Pt groups lead to formation of a complete helical loop in the molecule so that the terminal carboxylic acid groups lie *anti* to one another, despite the presence of the non-linear bridging

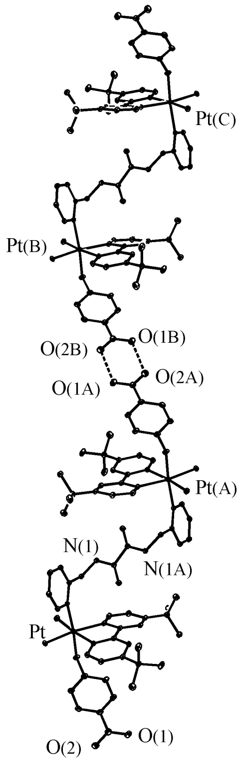


Fig. 1 Part of the zigzag polymer chain in complex **2**.

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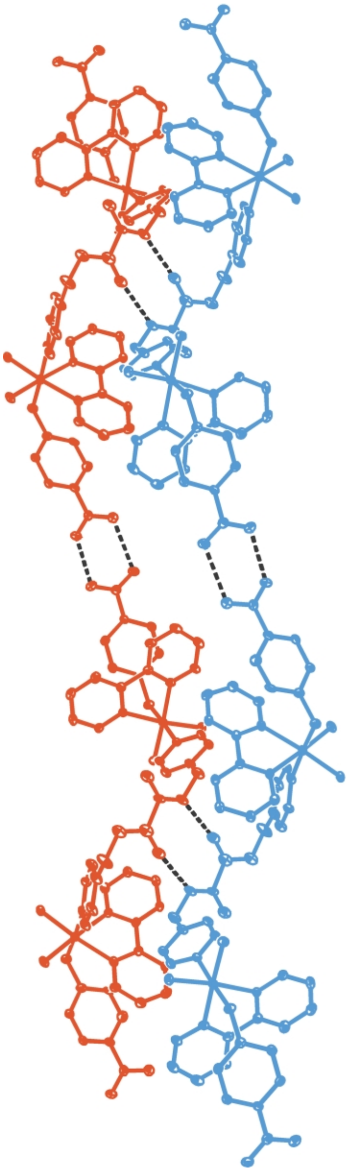

Fig. 2 The polymeric double helix structure of **3**, with individual chains shown in blue and red. The *tert*-butyl groups are omitted for clarity.

group. The dication has approximate C_2 symmetry, but there is no crystallographically imposed symmetry. The result is that each polymer chain is isotactic (*PPP*... or *MMM*...), with the pitch of the helix at 26.1 Å.

One of the amide NH groups of each cation **3** hydrogen bonds weakly to a hexafluorophosphate anion, and so is not available for inter-amide group hydrogen bonding, but the atoms N(98) and O(90) of the diamide bridge are available for intermolecular hydrogen bonding between cationic complexes. This pairwise head-to-tail, $R_2^2(10)$, hydrogen bonding occurs with equivalent amide groups in a neighbouring chain, with O(90)···N(98A) = O(90A)···N(98) = 2.75 Å. Molecules connected by these amide···amide hydrogen bonds are related by a center of symmetry and so have opposite helicity (*P*,*M*). Fig. 2 shows four units of the infinite structure that results from the overall self-assembly. It is not possible for pairs of homochiral helices of opposite helicity to form a conventional double helix, and the structure shown in Fig. 2 can be described as a side-by-side polymeric double helix, a new structural motif. The association between helical chains is comparable to that in oligomeric, organic "zipper" compounds, which are models for self-replication or muscle action but whose helicity is not known.[6] There is also a resemblance to inorganic or organic ladder structures, in which a variety of crosslinking groups can be used, but which are usually designed with linear rather than helical rails.[1,2]

The ^{1}H or ^{13}C NMR spectrum of **3** in CH_2Cl_2 solution at room temperature contained only one MePt resonance, indicating easy inversion of helicity. However, at 193 K, the methylplatinum resonance was very broad in the ^{1}H NMR and two resonances were resolved in the ^{13}C NMR for the $PtMe^aMe^b$ groups, indicating that helicity is present. So far as we are aware, no other organometallic double helices are known, and this work further illustrates how the biomimetic approach of introducing amide units into the molecular building blocks can lead to interesting new structural forms of polymers by self-assembly.[1-5,7]

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Notes and references

† *Synthesis* of **3**: a mixture of $[PtMe_2(bu_2bipy)]$ (100 mg) and α-bromo-4-toluic acid (44 mg) in acetone (50 mL) was stirred for 1 h at room temperature. To this solution was added dropwise a solution of $AgPF_6$ (51 mg) in acetone (5 mL) to precipitate AgBr. After 30 min, the mixture was filtered into a solution of *N*,*N*-bis(pyridin-4-ylmethyl)oxalamide in acetone (5 mL). The solvent was evaporated under vacuum and the product was recrystallized using acetone–pentane. Yield: 87%. Selected NMR data in acetone-d_6: (^{1}H) = 1.38 [s, 12H, ^2J(PtH) 66 Hz, PtMe]; 1.39 [s, 36H, Bu]; 2.99 [s, 4H, ^2J(PtH) 92 Hz, $PtCH_2$]; 4.42 [d, 4H, $^3J(CH_2NH)$ 6 Hz, CH_2]. *Crystal data* for $\mathbf{3}[PF_6]_2\cdot 1.5Me_2CO$: $C_{74.5}H_{94}F_{12}N_8O_{7.50}P_2Pt_2$, M_r = 1901.70, T = 200 K, λ = 0.71073 Å, triclinic, $P1$, a = 16.3333(4), b = 16.6092(5), c = 17.8427(5) Å, α = 98.680(1), β = 106.840(1), γ = 91.364(1)° , V = 4568.1(2) Å^3, Z = 2, D_c = 1.383 Mg m^{-3}, $R1$ = 0.0622, $wR2$ = 0.1502 [$I > 2\sigma(I)$]. Complex **2** was prepared similarly. *Crystal data* for $\mathbf{2}[PF_6]\cdot 1.5CH_2Cl_2$: $C_{36.50}H_{47}Cl_3F_6N_4O_3PPt$, M_r 1036.19, T = 200 K, λ = 0.71073 Å, triclinic, P1, a = 11.6287(2), b = 11.7868(2), c = 16.3564(3) Å, α = 105.562(1), β = 101.923(1), γ = 93.436(1)°, V = 2097.23(6) Å^3, Z = 2, D_c = 1.641 Mg m^{-3}, $R1$ = 0.0482, $wR2$ = 0.1029 [$I > 2\sigma(I)$]. CCDC reference numbers 183211 and 183212. See http://www.rsc.org/suppdata/cc/b2/b203183c/ for crystallographic data in CIF or other electronic format.

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