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An organometallic polyrotaxane and a new type of polyrotaxane architecture

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A new architecture, comprising two interpenetrating chains of rings, has been discovered in the first organometallic polyrotaxane; the synthesis combines the techniques of organometallic chemistry, coordination chemistry and self-assembly through hydrogen bonding.

Functional polymers having novel architectures are of great current interest and polyrotaxanes are viewed as particularly significant. Admirable synthetic strategies have been developed to polymers with the rotaxanes on the main chain or side chain,[1–5] (**A** and **B** in Chart 1), and potential applications ranging from drug delivery vehicles[6] to sensor devices[7–9] have been identified. If polymeric chains also contain ring components, then interpenetration can occur and this has been demonstrated in a two-dimensional sheet polyrotaxane (**C** in Chart 1).[10] This paper describes a new polyrotaxane architecture in which a related form of interpenetration occurs to give a one-dimensional polyrotaxane of type **D** (Chart 1). The synthesis involves introduction of a hydrogen-bonding group by oxidative addition (organometallic chemistry), assembly of three of these units at a tridentate templating ligand (coordination chemistry) and then formation of the polyrotaxane product by self-assembly through the hydrogen-bonding substituents. The combination of these interdisciplinary methods has great potential for forming new functional materials but has very rarely been used in the past.[11,12]

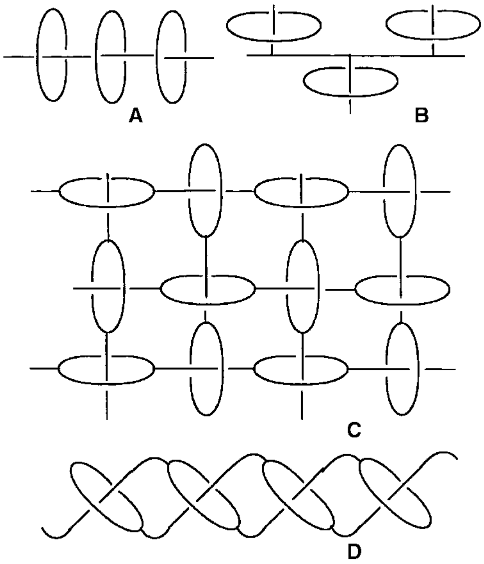
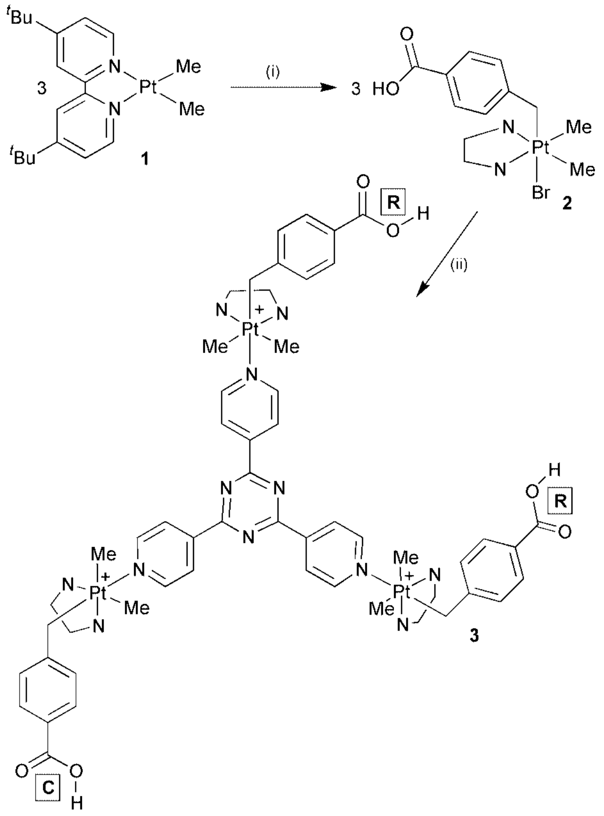


Chart 1 Polyrotaxanes.

The reaction of $[PtMe_2(Bu_2bipy)]$, **1**, (Bu_2bipy = 4,4′-di-*tert*-butyl-2,2′-bipyridine)[11] with α-bromo-4-toluic acid gave the complex $[PtBrMe_2(Bu_2bipy)(CH_2C_6H_4CO_2H)]$, **2**, containing a carboxylic acid functional group designed to take part in intermolecular hydrogen bonding (Scheme 1). Three of these organoplatinum(IV) units were assembled at a tridentate ligand by substitution of bromide ligands by the pyridyl donors of *sec*-tris(4-pyridyl)triazine, Py_3T, which is known to give interesting structures in coordination chemistry.[13] The bromide abstraction step in the synthesis was effected by use of $AgPF_6$, to give the product $[\{(HO_2CC_6H_4CH_2)(Bu_2bipy)Me_2Pt\}_3\{(\beta\text{-}NC_5H_4)_3(C_3N_3)\}]^{3+}$, **3**, as the hexafluorophosphate salt. In the successful crystallization, 0.5 equiv. of HPF_6 and five acetone molecules were incorporated for each complex **3**$[PF_6]_3$.[14]

The ions **3** self-assemble into chains of rings in the following way: the two carboxylic acid groups labelled **R** in Scheme 1 hydrogen bond to the group of a neighbouring molecule to form 56-membered rings and the group labelled **C** hydrogen bonds to the equivalent carboxylic acid group of a second neighbouring molecule to make a chain. Part of the one-dimensional polymer, comprised of rings connected by chains, that results from this self-assembly is illustrated in Fig. 1. Most remarkably, two of these polymeric units interpenetrate, with each ring section of one polymer penetrated by the chain section of the other, to form a new type of polyrotaxane (**D**, Chart 1) as illustrated in Fig. 2.

The infrared spectrum of **3** as a Nujol mull contains peaks due to ν(O–H) in the range 2545–2672 cm^{-1}, and the O···O distances between the hydrogen-bonded carboxylic acid groups in **3** are in the range 2.6–2.7 Å, Fig. 1, indicating the presence



Scheme 1 NN = Bu_2bipy. *Reagents*: (i) 3 $BrCH_2C_6H_4CO_2H$; (ii) 3 Ag^+, $C_3N_3(C_5H_4N)_3$, $-AgBr$.

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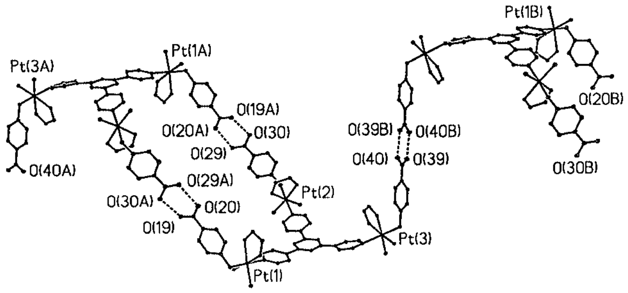

Fig. 1 The structure of complex **3**. The hydrogen bonding to give chains [O(39)···O(40B) = 2.60 Å] of rings [O(20)···O(29A) = 2.64 Å, O(19)···O(30A) = 2.70 Å] is illustrated for a central molecule and its two neighbours. Only the NCCN atoms of the Bu_2bipy ligands are shown for clarity.

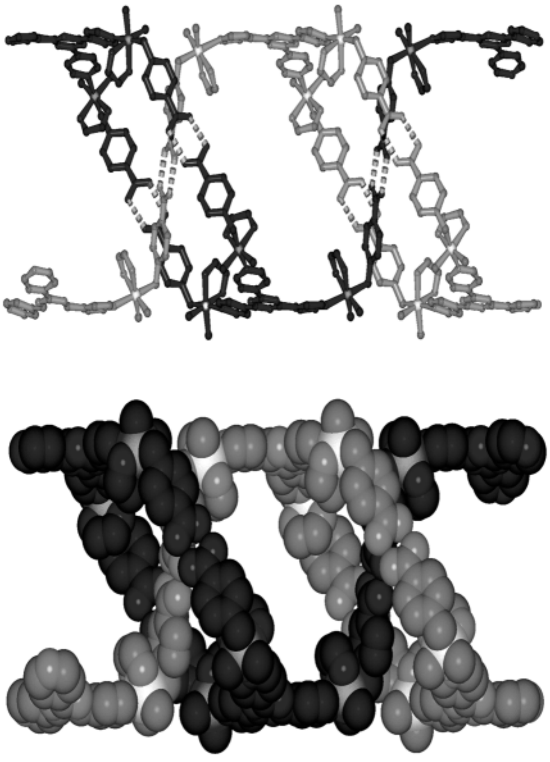

Fig. 2 A section of the polyrotaxane structure formed by two interpenetrating polymer units; only the central NCCN atoms of the Bu_2bipy ligands are shown for clarity. Above, ball and stick and, below, space filling representations.

of strong hydrogen bonds.[15] Are these hydrogen bonds maintained in solution? In acetone-d_6 solution, the ^{1}H NMR spectrum of **3** contains two methylplatinum resonances and two *tert*-butyl resonances in an approximately 2:1 intensity ratio, that are tentatively assigned to organoplatinum units within rings and chains respectively, suggesting that at least fragments of the structure are maintained in solution.

Complex **3** appears to be the first organometallic polyrotaxane and it has a unique structure of type **D** (Chart 1). Its formation involves three easy steps, using organometallic chemistry to introduce the hydrogen bonding group, coordination chemistry to assemble three hydrogen bonding groups around a central bridging ligand, and then the final self-assembly of the polyrotaxane through hydrogen bonding. Similar procedures have the potential to lead to many new and interesting forms of molecular architecture.

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14 *Crystal data* for complex **3**$[PF_6]_3 \cdot 0.5H[PF_6] \cdot 5Me_2CO$: $C_{117}H_{153.50}F_{21}N_{12}O_{11}P_{3.50}Pt_3$, M = 2996.68, triclinic, space group $P\bar{1}$, a = 18.9270(4), b = 19.1763(4), c = 21.8457(5) Å, α = 103.335(1), β = 97.786(1), γ = 118.221(1)°, V = 6515.6(2) Å^3, Z = 2, D_c = 1.527 Mg m^{-3}, T = 200 K, μ = 3.344 mm^{-1}, no. of reflections 63523, R_1 [$I > 2\sigma(I)$] = 0.0506, wR_2 = 0.1318. Partial (disordered) protonation of N(72) of the triazine is thought to occur; the proton was tentatively located in this position and appears to participate in H-bonding. CCDC reference number 164614. See http://www.rsc.org/suppdata/cc/b1/b103967a/ for crystallographic data in CIF or other electronic format. NMR in acetone-d_6: (^{1}H) = 1.38, 1.40 [s, 54H, Bu]; 1.44, 1.48 [s, 18H, ^2J(PtH) = 66, 71 Hz, PtMe]; 3.09, 3.11 [s, 6H, ^2J(PtH) = 92, 93 Hz, $PtCH_2$]. IR (Nujol mull): ν(CO) = 1613, 1701 cm^{-1}; ν(OH) = 2547, 2672 cm^{-1}.

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