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The First Coordinatively Saturated, Quadruply Stranded Helicate and Its Encapsulation of a Hexafluorophosphate Anion.**

David A. McMorran* and Peter J. Steel*

The use of metal ions to control the self-assembly of discrete supramolecular species has been an area of intense interest for some years,[1] with helicates having received particular attention.[2, 3] This interest has been driven, at least in part, by the potential use of helicates as functional components of molecular devices.[2] Although single-, double- and triple-stranded helicates have been well-documented,[2, 4] to our knowledge the only example of a quadruply stranded helicate is the recent report of pentanuclear metal complexes bridged by a pentadentate ligand.[5] These species contain metal – metal bonds with terminal ancillary ligands on octahedral metal centers and, as such, can be classified as unsaturated helicates.[2] It was predicted[2] that the synthesis of a saturated quadruply stranded helicate might be achieved by employing a combination of square-planar metal centers with oligomonodentate bridging ligands. We now report the successful realization of this challenge, with the synthesis and X-ray crystal structure of a quadruply stranded helicate that encapsulates a hexafluorophosphate anion.

We have previously reported that reaction of 1,4-bis(2-pyridyloxy)benzene with silver nitrate results in the self-assembly of a M_2L_2 dimetalloparacyclophane with intimate $\pi-\pi$ stacking of the central benzene rings,[6] whilst replacement of the central *p*-phenylene ring with a 2,7-naphthylene spacer results in the formation of a M_2L_4 molecular box.[7] In order to change the topology of the ligand so as to enlarge the cavity within such metallosupramolecular species we have begun to examine the coordination chemistry of the 3-pyridyl analogues. Thus, the ligand 1,4-bis(3-pyridyloxy)benzene (**1**) was prepared (Scheme 1) by reaction of 3-hydroxypyridine with 1,4-dibromobenzene in the presence of potassium carbonate and copper bronze.[8] Reactions of **1** with $[PdCl_2(PPh_3)_2]$ and $[PdI_2(py)_2]$ (py = pyridine), in the presence of silver triflate, gave what we believe to be the dimeric complexes **2** and **3**, respectively, the formulations of which are supported by their elemental analyses, ^1H NMR and FAB mass spectra (see Experimental Section). Diffusion of diethyl ether into an acetonitrile solution of **3** containing ammonium hexafluorophosphate resulted in a reorganization of the components and the assembly of a M_2L_4 species (**4**), which deposited from the solution as a tetrakis(hexafluorophosphate) salt and as a bis(acetonitrile) solvate. This latter species was prepared more efficiently, in 70% yield, when the appropriate 2:1 ligand:metal stoichiometry was employed.

A single crystal X-ray structure determination was carried out to determine the structure of this compound unambiguously.[9] The compound crystallizes in the centrosymmetric space group $P2_1/n$, the asymmetric unit of which contains a full M_2L_4 helical cage (**4**) that has each square-planar palladium atom coordinated to the four bridging ligands and within which resides a well-ordered PF_6^- ion (Figure 1). External to the cage are three other PF_6^- anions (two of which are disordered) and two acetonitrile solvate molecules (not shown). The dimensions of the cage are defined by the Pd···Pd separation [8.8402(8) Å] and the distance between the centroids of the cofacial benzene rings [8.849(7) and 8.925(7) Å].

Figure 2 shows the cage viewed down the Pd – Pd axis, which serves to emphasize its approximate D_4 symmetry and the helical disposition of the ligands. The helical pitch is defined by the approximate 45° angle subtended by each ligand about the helical axis. The planes of the pyridine rings are all approximately orthogonal to the planes of the linking benzene rings. This cage can be classified as a saturated,

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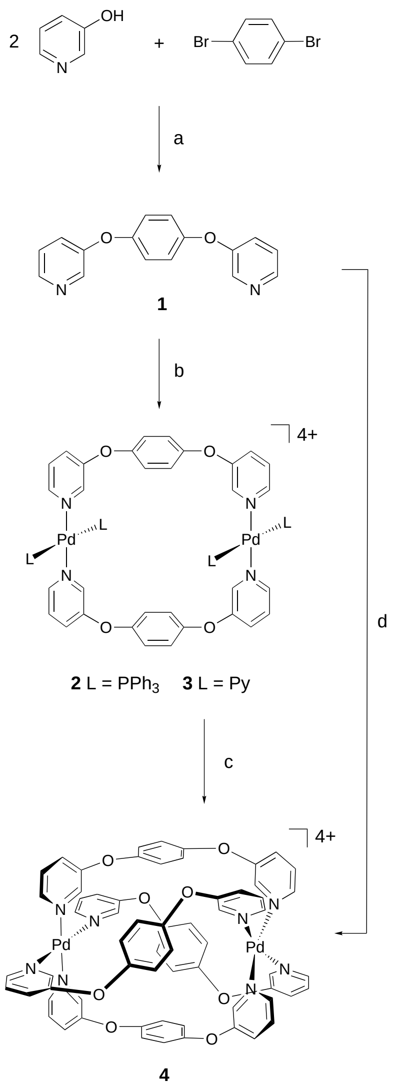

Scheme 1. Preparations of **1**–**4**. a) K_2CO_3, Cu^0, dimethylacetamide, heat; b) **2**: $[PdCl_2(PPh_3)_2]$, AgOTf, CH_2Cl_2, **3**: $[PdI_2(Py)_2]$, AgOTf, acetone, NH_4PF_6; c) MeCN/Et_2O; d) 0.5 equiv $[PdI_2(Py)_2]$, AgOTf, MeCN, NH_4PF_6. OTf = Trifluoromethanesulfonate (triflate).

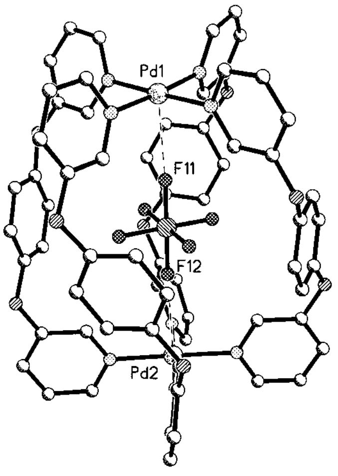

Figure 1. Perspective view of the helicate **4** and its encapsulated PF_6^- ion. Selected interatomic distances [Å] and angles [°]: Pd–N 2.008(6)–2.032(5), P1–F 1.565(5)–1.582(5), Pd1–F11 2.789(5), Pd2–F12 2.911(5); Pd1–Pd2 8.8402(8); N-Pd-N 87.1(2)–92.5(2)/176.4(2)–179.0(2), Pd1-F11-P1 176.4(4), Pd2-F12-P1 176.3(3).

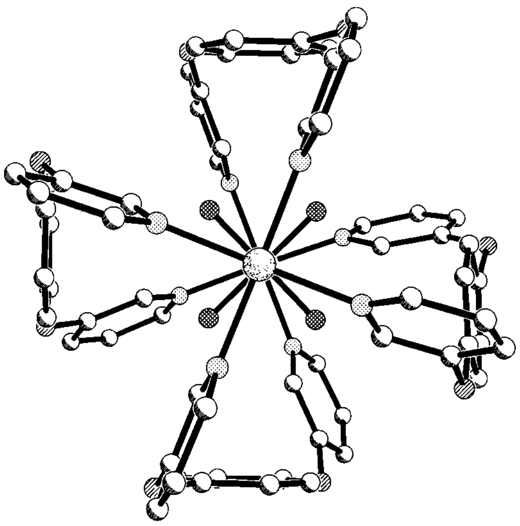

Figure 2. View of $[\mathbf{4}(PF_6)]^{3+}$ down the helical Pd–Pd axis.

homotopic, quadruply stranded helicate on the basis of the definitions of Piguet et al.,[2] and is the first such example.

A remarkable feature of the stucture is the encapsulation of the hexafluorophosphate anion. In contrast to the many molecular hosts capable of recognizing and complexing cationic guests, the search for similar species capable of complexing anionic guests has proved considerably more difficult.[10] Cryptates have long been known to encapsulate simple anions such as halide[11] and azide,[12] but only more recently have they been definitively shown to complex oxyanions and perfluoroanions.[13] Some metallosupramolecular species have been shown to act as hosts for neutral,[14] cationic,[15] and anionic[16] guests. Whereas cation encapsulation by triple helicates has been described,[15, 17] only one example of anion encapsulation by a helicate has been reported, this being a chloride ion enclosed by a circular double helicate.[18] Thus, the present example represents the first case of encapsulation of a polyatomic anion by a helicate and only the second crystallographically characterized example of encapsulation of a hexafluorophosphate anion by any species.[19]

Although PF_6^- ions normally act as noncoordinating anions,[20] the encapsulated anion within the cage **4** makes weak contacts with the palladium centers [Pd1–F11 = 2.789(5); Pd2–F12 = 2.911(5) Å], as indicated by the dashed lines in Figure 1. The four remaining fluorine atoms reside in the spaces between the faces of the four benzene rings. It is notable that this is the first crystallographically characterized example in which a hexafluorophosphate anion acts as a bridging ligand between two metal centers.[20]

Evidence for the fact that this structure is maintained in solution is provided by the observation that dissolution of the crystals in DMSO gives a solution that gives rise to a ^1H NMR spectrum consistent with the X-ray structure and, most importantly, a ^{19}F NMR spectrum that shows two doublets for the PF_6^- ions. This suggests that, on the timescale of the NMR experiment, the PF_6^- ion remains encapsulated within the helicate, but is tumbling within the cavity, rather than being locked in one orientation as in the solid state X-ray structure. Experiments are underway to determine whether the PF_6^- ion can be exchanged for other anions and, therefore, how generally or selectively this molecular cage can act as a host for anions.

Experimental Section

2: $[PdCl_2(PPh_3)_2]$ (1 equiv) and AgOTf (2 equiv) were stirred in dichloromethane/acetonitrile (9/1) for 30 min. The AgCl was filtered off, the solvent removed, and the residue extracted with dichloromethane. This solution was filtered and stirred overnight with **1** (1 equiv). The solvent was then removed, the residue dissolved in chloroform (ca. 2 mL), and diethyl ether added. The resulting pale yellow solid was filtered off, washed with diethyl ether and dried in vacuo. Yield 84%; m.p. 182–184 °C (decomp); elemental analysis calcd for $C_{108}H_{84}P_4N_4O_{16}F_{12}S_4Pd_2 \cdot CHCl_3$: C 52.23, H 3.41, N, 2.23; found: C 52.99, H 3.64, N 2.65; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.52$ (s, 8H, H2,3,5,6), 6.99 (m, 8H, H4′,5′), 7.41 (m, 36H, *m*, *p*-PPh_3), 7.68 (dd, 24H, *o*-PPh_3), 8.49 (s, 4H, H2′), 8.88 (d, 4H, H6′); FAB-MS: *m/z*: 1976 $[M - 3(OTf)]^+$.

3: $[PdI_2(py)_2]$ (1 equiv) and AgOTf (2 equiv) were stirred in acetone for 30 min. The AgI was filtered off and the filtrate was stirred overnight with **1** (1 equiv). NH_4PF_6 (10 equiv) was added and the solvent was then removed. The residue was extracted with dichloromethane (ca. 2 mL), filtered, and diethyl ether added. The resulting pale yellow solid was filtered off, washed with diethyl ether and dried in vacuo. Yield 85%; m.p. > 210 °C (decomp); elemental analysis calcd for $C_{52}H_{44}N_8O_4P_4F_{24}Pd_2 \cdot CH_2Cl_2$: C 36.95, H 2.69, N 6.50; found: C 36.51, H 2.72, N 6.73; ^1H NMR (300 MHz, CD_3CN): $\delta =$ 7.00 (s, 8H, H2,3,5,6), 7.64 (t, 8H, py-H3,5), 7.77 (dd, 4H, H5′), 7.91 (d, 4H, H4′), 8.09 (t, 4H, py-H4), 8.62 (s, 4H, H2′), 8.85 (d, 8H, py-H2,6), 8.64 (d, 4H, H6′); FAB-MS: *m/z*: 1493 $[M - (PF_6)]^+$. Recrystallization of an acetonitrile solution of **3** by diethyl ether infusion gave cream crystals of $[\mathbf{4} \cdot (PF_6)_4 \cdot 2\,CH_3CN]$, suitable for X-ray diffraction.

4: $[PdI_2(py)_2]$ (1 equiv) and AgOTf (2 equiv) were stirred in dichloromethane/acetone (9/1) for 30 min. The AgI was filtered off, the solvent removed, and the residue extracted with dichloromethane. This solution was filtered and the solvent removed. The residue was then dissolved in acetonitrile and stirred overnight with **1** (2 equiv) and NH_4PF_6 (10 equiv). The solvent was then reduced to ca. 1 mL, chloroform (ca. 5 mL) and water (ca. 5 mL) were added and the off-white solid filtered off, washed with water, ethanol, and diethyl ether, and dried in vacuo. Yield 70%; m.p. > 250 °C (decomp); elemental analysis calcd for $C_{64}H_{48}N_8O_8P_4F_{24}Pd_2 \cdot 2\,H_2O$: C 40.75, H 2.78, N 5.94; found: C 40.65, H 2.57, N 6.41; ^1H NMR (300 MHz, $[D_6]$DMSO): $\delta = 6.93$ (s, 16H, H2,3,5,6), 7.85 (dd, 8H, H5′), 8.01 (d, 8H, H4′), 8.42 (s, 8H, H2′), 9.14 (d, 8H, H6′); FAB-MS: *m/z*: 1704.8 $[M - PF_6]^+$, 1559.8 $[M - 2(PF_6)]^+$.

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