Mono-palladium(II) complexes of diamidopyridine–dipyrromethane hybrid macrocycles†

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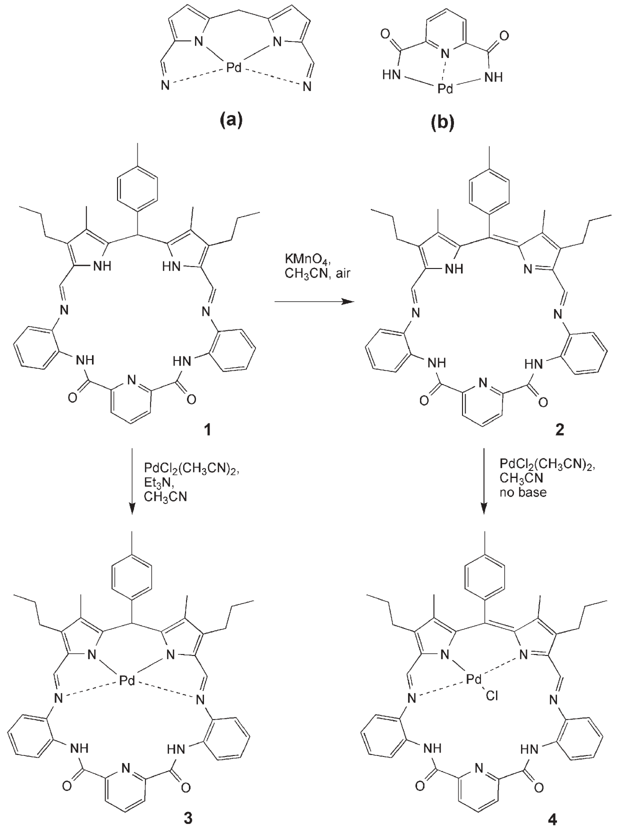
The reaction of diamidopyridine–dipyrromethane or dipyrromethene hybrid macrocycles with palladium(II) affords monometalated complexes, wherein the metal centre is coordinated to the macrocycle exclusively through pyrrolic nitrogen donor atoms.

In recent years Schiff base oligopyrrolic macrocycles, a special class of expanded porphyrins, have attracted considerable attention in part because they display a rich coordination chemistry.[1,2] To date, imine-containing oligopyrrole macrocycles have been used to stabilize complexes containing high-valent actinide oxo cations, trivalent lanthanide centers, and several different first-row transition metals.[3] A limited number of binuclear metal complexes have also been prepared using Schiff base expanded porphyrins.[1e,2,3] Recently we described a new class of hybrid diamidopyridine–dipyrromethane macrocycles and showed that the diiminodipyrromethane fragment could be selectively oxidized to produce the corresponding conjugated diiminodipyrromethene system (Scheme 1, structures **1** and **2**).[4] Both macrocycles proved effective as anion binding agents. However, their cation complexation chemistry was not explored. Nonetheless, these two systems (compounds **1** and **2**) are of interest in this latter context because they contain two potential binding sites for cation coordination, namely diiminodipyrromethane(methene) and diamidopyridine fragments. 5,5′-Diiminodipyrrole fragments are attractive because they can provide the same 4*N*-coordinate metal ligation as porphyrin, albeit in a very different structural environment; by contrast, the diamidopyridine subunit is of interest because it can potentially stabilize 3*N*-coordinate complexes with a donor set that bears little resemblance to porphyrins. To date, complexes of palladium(II) have been stabilized using receptors containing both individual fragments, specifically by Love *et al.*[5] and Hirao *et al.*,[6] respectively. However, to the best of our knowledge no system has been studied wherein both motifs are contained within a single macrocycle and thus allowed to "compete" for the same cation. In this paper we report the cation coordination properties of ligands **1** and **2** with palladium(II) and show that under conditions of normal metal insertion, the resulting complexes have the metal center coordinated to the macrocycles exclusively through pyrrolic nitrogen donor atoms.



Scheme 1 Structures of building blocks, diiminodipyrromethane (a) and 2,6-diamidopyridine (b), showing the coordination environment for Pd(II) complexation. Oxidation of a dipyrromethane fragment **1** to the corresponding dipyrromethene **2**, and the synthesis of two distinct mono-palladium(II) complexes.

Reaction of **1** or **2** with Pd(OAc)$_2$ in acetonitrile or dichloromethane using either 1 or 2 equiv. of the metal salt produces a mixture of mono- and binuclear complexes according to ESI mass spectrometry. The binuclear complexes appeared to be unstable and their apparent decomposition made difficult the separation of the corresponding mononuclear complexes. However, using one equivalent of dichlorobis(acetonitrile) palladium(II) salt as the Pd(II) source and carrying out the insertion in the presence of triethylamine led to the formation of the mono-palladium(II) complex **3** in 81% yield. In contrast, the metallation of ligand **2** could only be effected readily in the absence of base, yielding the mono-palladium(II) complex **4** in 60% yield.

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Based on an analysis of the spectroscopic and crystallographic data,‡ the palladium(II) cation is coordinated selectively within the diiminodipyrrole environment in the case of both complexes **3** and **4**.

In the ^{1}H NMR spectrum (CD_2Cl_2, room temperature) of complex **3**, all the signals are broadened except the AA′BB′ pattern ascribed to the tolyl group. At −50 °C, the signals are sharp and correspond to an unsymmetrical structure, wherein the two characteristic signals of the amido 1H protons appear as a broad peak at 10.9 ppm and a sharp signal at 8.4 ppm, as inferred from an ^{1}H-^{13}C HSQC NMR experiment. These signals disappear upon treatment with D_2O. All NMR spectroscopic data are consistent with the suggestion that **3** undergoes self-association to produce aggregates containing several molecules of the complex in dichloromethane solution and that this aggregation process is substantially enhanced when the solution is cooled to −50 °C. In contrast, the peaks ascribed to aggregation are absent from the corresponding ^{1}H NMR spectrum recorded in DMSO-d_6 at room temperature. In fact, sharp signals are observed, supporting the notion that no appreciable self-association takes place in this highly polar solvent. The self-association inferred from the ^{1}H NMR analyses in CD_2Cl_2, was explicitly confirmed in the solid state *via* a single crystal X-ray diffraction analysis. In particular, the complex is seen to form a dimer through a hydrogen bond network involving the amido groups from two different molecules within independent unit cells (Fig. 1).

The complexation of palladium locks the conformation of the ligand, such that the two amide NH protons are oriented in the same direction. One of the amide NH signals seen in the NMR spectrum recorded in CD_2Cl_2 resonates at lower field and is thought to participate in the hydrogen bonding interactions that stabilize the self-association process both in dichloromethane solution and in the solid state. According to the crystallographic data, two molecules of complex **3** are bound *via* a hydrogen bond involving O(1)···N(3) (separation: 2.792(6) Å). The palladium(II) cation is in square coordination environment with distances Pd–N(1), N(2), N(6), N(7) = 1.934(6), 2.108(6), 2.115(6), 1.943(6) Å, respectively. These bond lengths are similar to those in palladium porphyrin complexes but differs in N(1)–Pd–N(2) and N(2)–Pd–N(7) angles: namely 80 and 86 in **3** *vs.* 90, 90° in porphyrin complexes.[7]

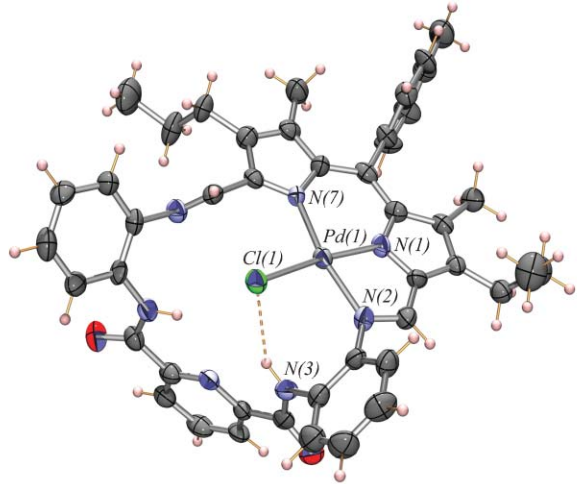

Fig. 2 Single crystal X-ray diffraction structure of complex **4** showing the hydrogen bond between chloride Cl(1) and the amido N(3)H hydrogen atoms (50% probability ellipsoids, solvent molecules are omitted for clarity).

According to the crystallographic data, complex **4** has an L-like conformation, with the two NH amido groups directed into the macrocycle cavity (Fig. 2). The palladium cation is in a square coordination environment, with the following palladium-to-nitrogen bond lengths and angles: Pd–N(7), N(1), N(2) = 2.042(5), 1.950(5), 2.073(5) Å, respectively, and N(7)–Pd–N(2) and N(2)–Pd–N(1) = 87 and 80°, respectively. The hydrogen bond between the amido group and the chloride anion is within normal limits, namely Cl(1)–N(3) = 3.099(5) Å. The presence of the metal cation presumably stabilizes the unsymmetrical ligand, an effect that is reflected in the NMR spectrum in solution. No evidence of association events is seen for complex **4**, either in solution or in the solid state.

Both mono-palladium complexes appeared to be rather stable in air. The UV-vis spectrum of complex **3** has two characteristic

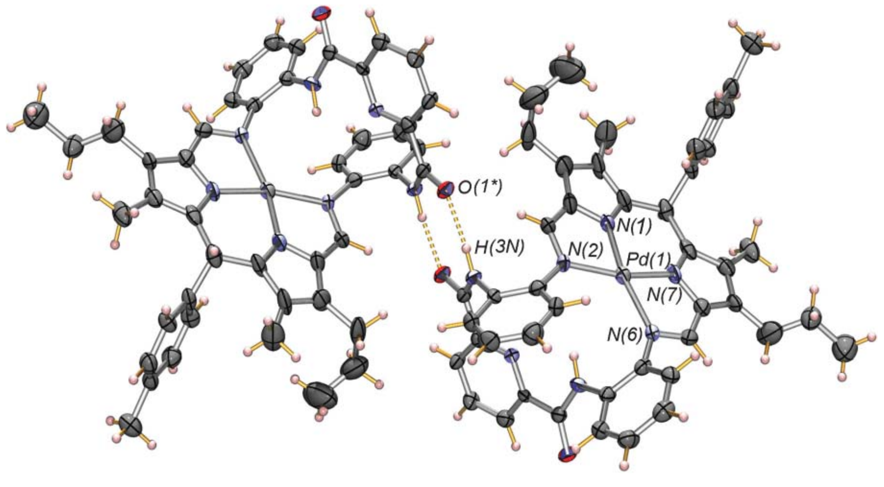

Fig. 1 Structure of the dimer of complex **3** showing the formation of two hydrogen bonds between the molecules (50% probability ellipsoids; solvent molecules are omitted; carbon atoms are shown in grey, nitrogen in blue, hydrogen bonds in orange and hydrogen atoms in pink). O(1*)—symbol indicates an atom at equivalent position (−*x*,−*y*,1 − *z*).

bands at 327 and 433 nm, with shoulders at 358 and 455 nm, respectively. Complex **4**, which contains a conjugated diiminodipyrromethene moiety gives rise to bands at 319 and 445 nm; it also displays bands in the visible region at 615 and 655 nm.

Since the macrocycles have two potential binding sites for metal cations, we attempted to study the complexation of a second metal cation to the diamidopyridine moiety. Using both mild metal insertion conditions (acetate or chloride salts of metal cations in the presence of an organic base) with the range of transition metal cations, including Pd(II), as well as deprotonation with strong base followed by reaction with metal salts, failed to produce bimetallic complex. Only polymeric products and products of decomposition were seen in the case of complexes **3** and **4**. The inaccessibility of bimetallic complexes leads us to suggest that complex **3** is unable to adopt a conformation appropriate for coordinating a second metal cation, a suggestion that is in accord with solution and solid state studies. In contrast, the inability of complex **4** to stabilize the complexation of a second cation is ascribed to its smaller size; the cavity simply cannot accommodate readily two metal cations without undue steric distortion or electrostatic repulsion.

During the course of these studies, we found that **3** can be oxidized to **4** quantitatively by treatment with $VOCl_3$ in THF. Moreover, we also found that complex **4** can be reduced to produce **3** by stirring a dichloromethane solution in the presence of triethylamine. This ligand-based redox chemistry of this complex resembles the behaviour seen for palladium(II) complexes bearing phosphine ligands, with the exception that the ligand (not palladium) is subject to two electron oxidation or reduction. This finding could make diiminodipyrrole–Pd type complexes of interest in catalytic studies. At present we are investigating the chemical reactivity of acyclic diiminodipyrrole palladium complexes. We are also targeting the preparation of more flexible analogous of ligands **1** and **2** with the goal of exploring further the metal coordination properties of this potentially generalizable class of hybrid macrocycles.

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Notes and references

‡ Crystal data. **3**: $C_{46.57}H_{46.24}Cl_{3.24}N_7O_2Pd$, M = 957.24, yellow lathes, 0.35 × 0.10 × 0.03 mm^3, triclinic, space group $P1$, a = 10.3506(4), b = 15.7321(5), c = 15.8708(6) Å, α= 60.823(2), β = 87.392(2), γ = 86.802(2)°, V = 2252.43(14) Å^3, Z = 2, ρ_c = 1.411 mg m^{-3}, μ = 0.650 mm^{-1}, $F(000)$ = 983, T = 153(2) K, Nonius Kappa CCD diffractometer, graphite monochromator with MoKα radiation, $R1$ = 0.0722, w$R2$ = 0.1279, 7817 independent reflections and 601 parameters. **4**: $C_{55}H_{63}ClN_8O_3Pd$ M = 1025.98, long dark-green needles, 0.42 × 0.08 × 0.07 mm^3, monoclinic, space group $C2/c$, a = 35.3431(8), b = 16.0453(6), c = 21.7368(7) Å, α = 90, β = 127.270(2), γ = 90°, V = 9809.5(5) Å^3, Z = 8, ρ_c = 1.389 mg m^{-3}, μ = 0.486 mm^{-1}, $F(000)$ = 4288, T = 153(2) K, Nonius Kappa CCD diffractometer, graphite monochromator with MoKα radiation, $R1$ = 0.0688, w$R2$ = 0.1421, 8607 independent reflections and 514 parameters. Data reduction were performed using DENZO-SMN. The structure was solved by direct methods using SIR97 and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97. SQUEEZE in PLATON98 was used to remove the contribution of the solvent to the structure factors. CCDC 615936 and 615937 for **3** and **4**, respectively. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b611946h

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