Agostic Pd$\cdots$H$^+\cdots$NHR$_2$ and Apical Pd$\cdots$NHR$_2$ Interactions: the Synthesis and Structures of [Pd^{II}Cl$_2$(H[9]aneN$_3$)]$^+$, the Pd^{II}–Pd^{II} Dimer [(H[9]aneN$_3$)Cl$_2$Pd–PdCl$_2$(H[9]aneN$_3$)]$^{2+}$, and [Pd(Me$_3$[9]aneN$_3$)(NCMe)$_2$]$^{2+}$†

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Long-range agostic Pd$\cdots$H$^+\cdots$NHR$_2$ interactions are observed in the crystal structure of the protonated form of *cis*-[Pd^{II}Cl$_2$([9]aneN$_3$)], while a direct apical Pd$\cdots$NHR$_2$ interaction is observed in the purple complex [Pd(Me$_3$[9]aneN$_3$)(NCMe)$_2$](PF$_6$)$_2$.

We have reported previously the synthesis, structures and redox properties of a series of d^8 Pd^{II} complexes such as [Pd([9]aneS$_3$)$_2$]$^{2+}$, [PdX$_2$([9]aneS$_3$)] (X = Cl, Br) and [Pd([9]aneS$_3$)(L)]$^{2+}$ (L = dppm, dppe, triphos, bipy, phen, 2PPh$_3$)† in which long-range apical interactions between the metal and an S-donor of [9]aneS$_3$ are observed.[1-3] Such interactions reflect the relatively large size, the softness, and the polarisability of thioether S-donors. It is noticeable that for aza macrocycles, the N-donor atoms appear not to form long-range interactions with Pd^{II} (or other metal ions); they tend either to form conventional M–N bonds or to be completely non-interacting to give dangling N atoms.[4-6] We wished to ascertain whether it was possible to generate long-range M$\cdots$N interactions by stereochemically and/or electronically forcing an N-donor to approach a square-planar d^8 metal centre. We report herein the generation and characterisation of such interactions in complexes of Pd^{II} with capping triaza macrocycles.

A suspension of PdCl$_2$ in H$_2$O adjusted to pH 9 with NaOH was treated with 1 equiv. of [9]aneN$_3$·3HCl at 50 °C for 1 h under N$_2$ to produce a yellow solution. Addition of NH$_4$PF$_6$, and NaOH to maintain the pH of the reaction solution at

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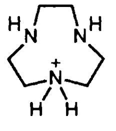
† *Abbreviations used*: [9]aneN$_3$ = 1,4,7-triazacyclononane; [9]aneS$_3$ = 1,4,7-trithiacyclononane; dppm = bis(diphenylphosphino)methane; dppe = 1,2-bis(diphenylphosphino)ethane; triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane; bipy = 2,2′-bipyridine; phen = 1,10-phenanthroline.



H[9]aneN$_3^+$

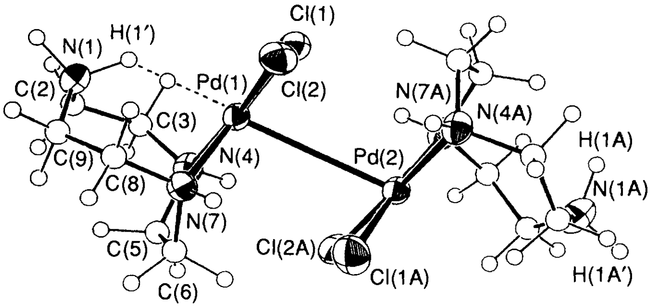


Fig. 1 View of the binuclear cation [(H[9]aneN$_3$)Cl$_2$Pd–PdCl$_2$(H[9]aneN$_3$)]$^{2+}$ with numbering scheme adopted. Pd(1)–Cl(1) 2.3260(14), Pd(1)–Cl(2) 2.2990(14), Pd(1)–N(4) 2.041(4), Pd(1)–N(7) 2.015(4), Pd(1)–H(1′) 2.296(4), Pd(1)–Pd(2) 3.3111(5), Pd(2)–Cl(1A) 2.2929(14), Pd(2)–Cl(2A) 2.3070(16), Pd(2)–N(4A) 2.061(4), Pd(2)–N(7A) 2.025(4) Å.

7.8–8.0, followed by cooling afforded yellow crystals of the product. The product is insoluble in common organic solvents but soluble in H$_2$O. The FAB mass spectrum of the complex showed peaks at m/z 613, 540 and 307 assigned to {[Pd(H[9]aneN$_3$)Cl$_2$]$_2$}$^+$, {[Pd(H[9]aneN$_3$)Cl]$_2$}$^+$ and {[Pd(H[9]aneN$_3$)Cl$_2$]}$^+$, respectively, suggesting a possible binuclear structure. A single-crystal structure determination‡ of the product confirms the presence of one binuclear cation [(H[9]aneN$_3$)Cl$_2$Pd^{II}–Pd^{II}Cl$_2$(H[9]aneN$_3$)]$^{2+}$, and two monomeric cations cis-[Pd^{II}(H[9]aneN$_3$)Cl$_2$]$^+$ within an extensive H-bonded network. These cations are associated in the crystal with two Cl$^-$ and two PF$_6^-$ counter-anions. In the dimer [(H[9]aneN$_3$)Cl$_2$Pd^{II}–Pd^{II}Cl$_2$(H[9]aneN$_3$)]$^{2+}$ (Fig. 1) each Pd^{II} is bound to two N-donors of the singly protonated (H[9]aneN$_3$)$^+$ macrocycle, and to two mutually *cis* Cl$^-$ ligands with a Pd–Pd distance of 3.3111(5) Å. The two pairs of Cl$^-$ ligands lie mutually *trans* to one another with respect to the Pd–Pd axis. However, the two (H[9]aneN$_3$)$^+$ macrocycles adopt different conformations. One (H[9]aneN$_3$)$^+$ has its protonated N atom inclined towards the Pd^{II} centre with one of the protons forming an agostic interaction with the Pd^{II} centre, Pd(1)–H(1′) = 2.296(4) Å. The second (H[9]aneN$_3$)$^+$ has its protonated N atom inclined away from the other Pd^{II} centre but forms an electrostatic interaction with a Cl$^-$ counter-ion (not shown in Fig. 1), H(1A′)–Cl(1X) = 1.982(5) Å. In each of the monomers (Fig. 2), the Pd^{II} centre is bound to two Cl$^-$ ligands and two N-donors in a square plane. In addition, however, an apical interaction with one of the protons of the unbound, protonated N atoms of (H[9]aneN$_3$)$^+$ is observed, Pd(3)–H(1B′) = 2.353(4), Pd(4)–H(1C′) =

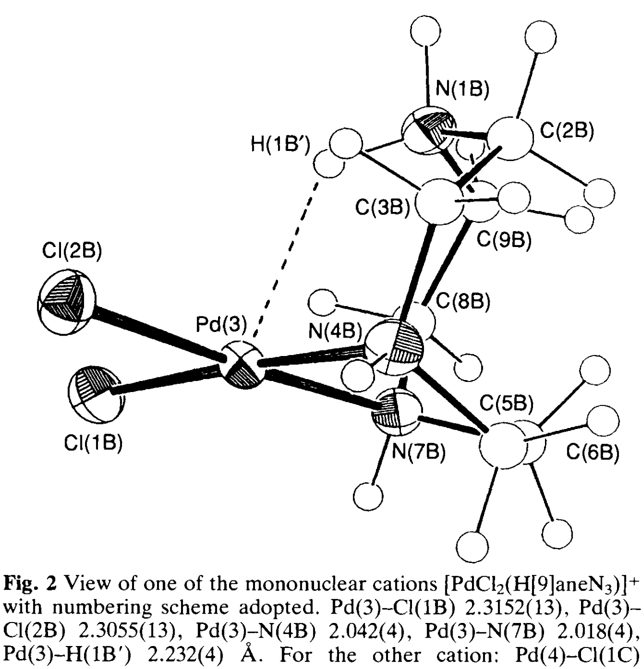


Fig. 2 View of one of the mononuclear cations [PdCl$_2$(H[9]aneN$_3$)]$^+$ with numbering scheme adopted. Pd(3)–Cl(1B) 2.3152(13), Pd(3)–Cl(2B) 2.3055(13), Pd(3)–N(4B) 2.042(4), Pd(3)–N(7B) 2.018(4), Pd(3)–H(1B′) 2.232(4) Å. For the other cation: Pd(4)–Cl(1C) 2.3220(14), Pd(4)–Cl(2C) 2.3000(15), Pd(4)–N(4C) 2.064(4), Pd(4)–N(7C) 2.008(4), Pd(4)–H(1C′) 2.401(4)Å.

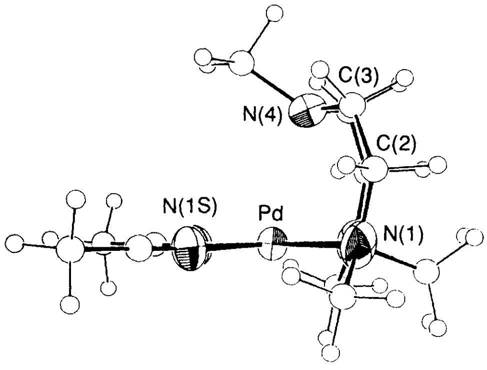


Fig. 3 View of the cation [Pd(Me$_3$[9]aneN$_3$)(NCMe)$_2$]$^{2+}$ with numbering scheme adopted. Pd–N(1) 2.037(7), Pd–N(1S) 2.016(6), Pd–N(4) 2.523(8) Å; ∠N(1)–Pd–N(4) 79.8(3), ∠N(1)–Pd–N(1S) 177.0(3), ∠N(4)–Pd–N(1S) 101.8(3)°.

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‡ *Crystal data* for: $C_{24}H_{64}Cl_{10}F_{12}N_{12}P_2Pd_4$, M = 1590.8, triclinic, space group $P\bar{1}$, a = 7.9510(11), b = 17.285(3), c = 19.730(3) Å, α = 74.423(11), β = 79.880(10), γ = 89.320(10)°, V = 2569 Å^3 [from 2θ values of 30 reflections measured at ±ω (2θ = 31–32°, $\bar{\lambda}$ = 0.71073 Å), T = 295 K], Z = 2, D_c = 2.056 g cm^{-3}, μ(Mo-Kα) = 2.026 mm^{-1}. A dark yellow columnar crystal was mounted on a Stoë Stadi-4 four-circle diffractometer. Data collection using Mo-Kα X-radiation ($\bar{\lambda}$ = 0.71073 Å) and ω–2θ scans gave 6985 reflections (2θ$_{max}$ 45°), of which 6294 with $F \geqslant 6\sigma(F)$ were used in all calculations. The structure was solved by automatic direct methods[10] and the solution developed using full-matrix least-squares refinement and difference Fourier synthesis. Anisotropic thermal parameters were refined for non-H atoms. Methylene H atoms were included in fixed, calculated positions;[11] those bound to N atoms were first located in a difference Fourier synthesis, and then included in fixed, calculated positions. Disorder in the PF$_6^-$ anions was modelled using partial occupancies for F atoms. At convergence, R = 0.0351, R_w = 0.0508, S = 3.141 for 593 parameters and in the final ΔF synthesis all residual features lay within the range −1.07 to 0.79 e Å^{-3}.

Crystal data for: $C_{13}H_{27}N_5Pd^{2+}2PF_6^-$, M = 649.6, orthorhombic, space group $Pnam$, a = 12.1179(9), b = 19.0834(5), c = 10.4381(7) Å, V = 2414 Å^3, Z = 4, D_c = 1.787 g cm^{-3}, T = 298K, μ(Mo-Kα) = 0.990 mm^{-1}. A purple acicular crystal was mounted on a Stoë Stadi-4 four-circle diffractometer. Data collection using Mo-Kα X-radiation ($\bar{\lambda}$ = 0.71073 Å) and ω–2θ scans gave 1838 unique reflections (2θ$_{max}$ 45°), of which 1267 with $F \geqslant 6\sigma(F)$ were used in all calculations. Following solution by heavy-atom methods, the structure was refined by full-matrix least-squares analysis (on F) but no unambiguous choice could be made between the possible space groups $Pnam$ and $Pna2_1$. Finally, a model was adopted which allowed two equally-occupied orientations for the macrocyclic ring in $Pnam$. Anisotropic thermal parameters were allowed for Pd, P, F and N atoms while macrocyclic H atoms were included in calculated positions and those in MeCN as part of a rigid group.[11] At final convergence, R = 0.0505, R_w = 0.0683, S = 1.096 for 139 parameters and the final ΔF synthesis showed no feature above 0.71 e Å^{-3}.

For both structures atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

2.401(4) Å. Thus, both binuclear and mononuclear cations show Pd···H$^+$···NHR$_2$ interactions. There is much current interest in the formation and properties of agostic H-interactions in C–H bonded systems.[7] However, few examples of interactions with N–H bonds have been characterised crystallographically,[8] and although the current example is not formally electron-deficient, the bonding can be rationalised *via* H$^+$ bridging between lone pairs on the N atom and the Pd^{II} d$_{z^2}$ orbital, $Pd \rightarrow H^+ \leftarrow NHR_2$.

Reaction of [Pd(NCMe)$_4$]$^{2+}$ with 1 equiv. of Me$_3$[9]aneN$_3$ in MeCN affords a purple solution. Addition of NH$_4$PF$_6$ gives [Pd(Me$_3$[9]aneN$_3$)(NCMe)$_2$](PF$_6$)$_2$ as a purple solid. The colour of this complex is reminiscent of the highly coloured complexes of Pd^{II} with thioether macrocycles, which show long-range apical Pd···S interactions, such as [Pd([9]aneS$_3$)(L)]$^{2+}$ (L = [9]aneS$_3$, bipy, phen).[1] Clearly, in the case of [Pd(Me$_3$[9]aneN$_3$)(NCMe)$_2$](PF$_6$)$_2$, the purple colour cannot be due to charge-transfer transitions involving S atoms.[9] The single crystal X-ray structure of [Pd(Me$_3$[9]aneN$_3$)(NCMe)$_2$](PF$_6$)$_2$ (Fig. 3) confirms a five-coordinate Pd^{II} centre, with two macrocyclic N-donors, Pd–N(1) = 2.037(7) Å, and two NCMe ligands, Pd–N(1S) = 2.016(6) Å bound in the equatorial plane. The third N-donor interacts at long range with the Pd^{II} centre, Pd–N(4) = 2.523(8) Å, to give a distorted square-based pyramidal structure.

Current work is aimed at synthesising further examples of H$^+$ and H$^-$ complexes of polyaza macrocyclic compounds.

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