Electronic Supplementary Information for Dalton Transactions

Supplementary Information

Platinum(II) and Palladium(II) Metallomacrocycles Derived from Cationic 4,4′-Bipyridinium, 3-Aminopyrazinium and 2-Aminopyrimidinium Ligands

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X-ray Diffraction Studies

Experimental

Data for **9**·NO_3 were collected with ω scans to approximately 56° 2θ using a Bruker SMART 1000 diffractometer employing graphite-monochromated Mo-K*a* radiation generated from a sealed tube (0.71073 Å) at 150(2) K. Data integration and reduction were undertaken with SAINT and XPREP.[1] Data for **8**·PF_6/OTf were collected on a Bruker-Nonius APEX2-X8-FR591 diffractometer employing graphite-monochromated Mo-Kα radiation generated from a rotating anode (0.71073 Å) with ω and ψ scans to at least 80° 2θ at 150(2) K.[2] Subsequent computations were carried out using the WinGX-32 graphical user interface.[3] Structures were solved by direct methods using SIR97.[4] Multi-scan empirical absorption corrections were applied to the data set using the program SADABS.[5] Data were refined and extended with SHELXL-97.[6] All ordered non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were included in idealised positions and refined using a riding model and nitrogen-bound were either first located in the difference Fourier map and refined with bond-length restraints or included in idealised positions and refined using a riding model. Disorder, were present, was modelled using standard crystallographic techniques including bond length and angle restraints where necessary to facilitate realistic models. Crystal and structure refinement data are summarised below.

1,3-Bis(1-methyl-2-aminopyrimidinium)benzene triflate hexafluorophosphate (8·PF_6/OTf)

Formula $C_{17.95}H_{18}F_{6.15}N_6O_{5.85}P_{0.05}S_{1.95}$, M 592.32, triclinic, space group $P\bar{1}$, *a* 9.6224(4), *b* 11.2521(5), *c* 12.3853(5) Å, α 98.435(2), β 112.739(2), γ 100.330(2)º, *V* 1181.73(9) Å^3, D_c 1.665 gcm^{-3}, *Z* 2, crystal size 0.300×0.250×0.200 mm, colour colourless, habit block, temperature 150(2) K, λ(MoKα) 0.71073 Å, μ(MoKα) 0.322 mm^{-1}, *T*(SADABS)$_{min,max}$ 0.859, 0.937, 2θ$_{max}$ 80.10, *hkl*

range -17 17, -20 20, -22 22, N 79449, N_{ind} 14574 (R_{merge} 0.0305), N_{obs} 12323(I > 2σ(I)), N_{var} 365,

residuals $R1(F)$ 0.0357, $wR2(F^2)$ 0.0982, GoF(all) 1.025, $\Delta\rho_{min,max}$ -0.384, 0.577 $e^{-}Å^{-3}$.

$w = 1/[\sigma^2(F_o^2)+(0.0496P)^2 + 0.2401P]$

Specific details:

The 5 % occupancy anion was modelled with identical isotropic thermal parameters for each atom.

Table S1. Hydrogen Bond Geometry for **8**·PF_6/OTf.

Donor	Hydrogen	Acceptor	D-H(Å)	H-A(Å)	D-A(Å)	DHA Angle(º)
N(2)	H(2A)	N(6)	0.88	2.28	3.1499(8)	171.7
N(2)	H(2B)	O(3)[1]	0.88	2.21	3.0602(9)	162.0
N(2)	H(2B)	S(1)[1]	0.88	2.86	3.5276(6)	133.9
N(5)	H(5C)	O(1)[1]	0.88	1.95	2.8205(8)	169.4
N(5)	H(5D)	O(5)	0.88	2.05	2.8436(9)	149.0
N(5)	H(5D)	F(11)	0.88	2.11	2.905(18)	150.1

Symmetry Operator:

[1] -x, -y, -z

1-Methyl-3-aminopyrazinium nitrate (9·NO_3)

Formula $C_5H_8N_4O_3$, M 172.15, trigonal, space group $P3_2$, *a* 6.1596(7), *b* 6.1596(7), *c* 16.966(4) Å, γ120.00º, *V* 557.46(16) Å^3, D_c 1.538 gcm^{-3}, *Z* 3, crystal size 0.600×0.570×0.560 mm, colour colourless, habit block, temperature 150(2) K, λ(MoKα) 0.71073 Å, μ(MoKα) 0.128 mm^{-1}, $T(\text{SADABS})_{min,max}$ 0.834, 0.931, $2\theta_{max}$ 56.58, *hkl* range -8 8, -8 8, -22 21, *N* 5431, N_{ind} 1771(R_{merge} 0.0190), N_{obs} 1740(I > 2σ(I)), N_{var} 116, residuals

*R*1(*F*) 0.0266, *wR*2(F^2) 0.0690, GoF(all) 0.983, $\Delta\rho_{min,max}$ -0.270, 0.164 e$^-$Å^{-3}.

$w = 1/[\sigma^2(F_o^2)+(0.0509P)^2 + 0.0552P]$; $P = (F_o^2 +2F_c^2)/3$

Specific details:

The absolute structure was established with the Flack parameter refining to 0.074(1).[7]

Table S2. Hydrogen Bond Geometry for **9**·NO_3.

Donor	Hydrogen	Acceptor	D-H(Å)	H-A(Å)	D-A(Å)	DHA Angle(º)
N(3)	H(1N)	O(2)[1]	0.8899(11)	2.049(5)	2.9191(15)	165.6(16)
N(3)	H(2N)	O(3)	0.8899(10)	2.176(5)	3.0433(14)	164.8(16)
N(3)	H(2N)	O(1)	0.8899(10)	2.482(11)	3.2135(15)	139.9(14)
N(3)	H(2N)	N(4)	0.8899(10)	2.679(4)	3.5507(15)	166.6(15)

Symmetry Operator:

[1] -y, x-y, z+2/3

Discussion

The mixed salt [apym(*m*-xylylene)apym](OTf)$_{1.95}$(PF$_6$)$_{0.05}$ formed as colourless crystals upon slow evaporation of a CD_3CN solution containing equimolar amounts of [Pt(dppp)(OTf)$_2$] and [apym(*m*-xylylene)apym](PF$_6$)$_2$ (**8**). An ORTEP representation is given in Fig S1.

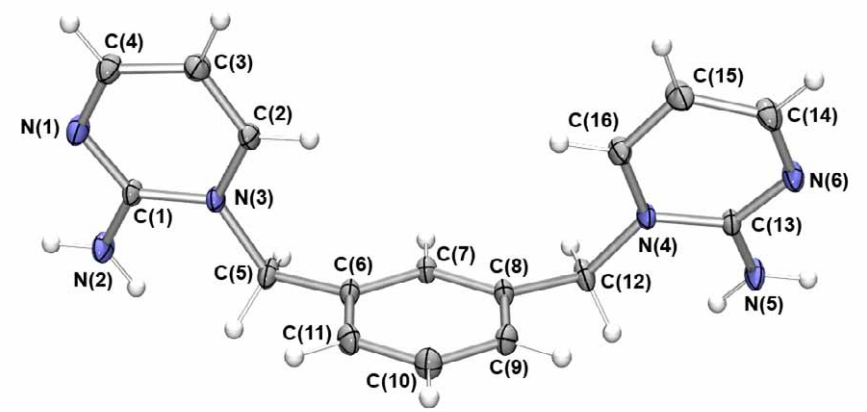

Figure S1: An ORTEP[8] representation of **8**·PF$_6$/OTf, with ellipsoids drawn at the 50% probability level. The OTf$^-$ and PF$_6^-$ anions are omitted for clarity.

There is a network of formal H-bonds present in the lattice (Table S1). These interactions exist both directly between adjacent ligands (N–H···N) and also between the ligands and OTf$^-$ anions (N–H···O). This arrangement results in the formation of 1D-polymeric chains, which propagate along the crystallographic *b*-axis (Fig S2). In turn, these chains are linked by C–H(phenylene)···O interactions to form 2-D sheets. The sheets are further linked by anion-π interactions (N(4) containing centroid–O(4) = 3.02 Å, N(3) containing centroid–F(6) = 2.99 Å). Interactions of this type have attracted recent attention due to their variable nature and their use in the binding of anions.[9]

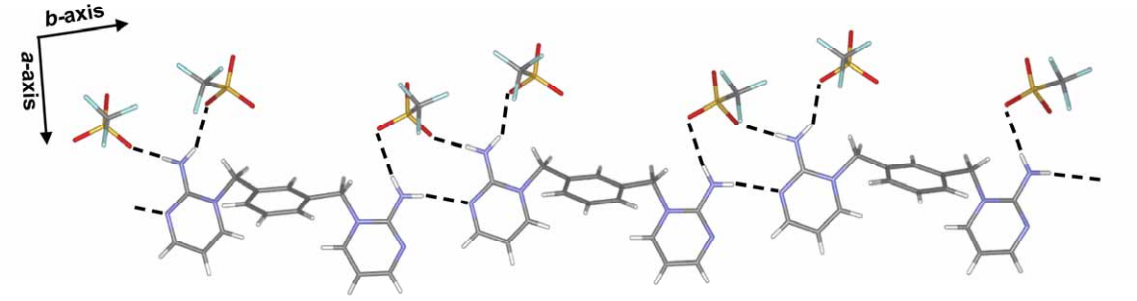

Figure S2: Schematic representation of the 1D-chains formed *via* H-bonding in the X-ray structure of **8**·PF_6/OTf. Dashed lines indicate H-bonds.

Slow evaporation of an aqueous solution containing **9**·NO_3 afforded colourless single crystals, crystallographic analysis of which resulted in the molecular structure shown in Figure S3.

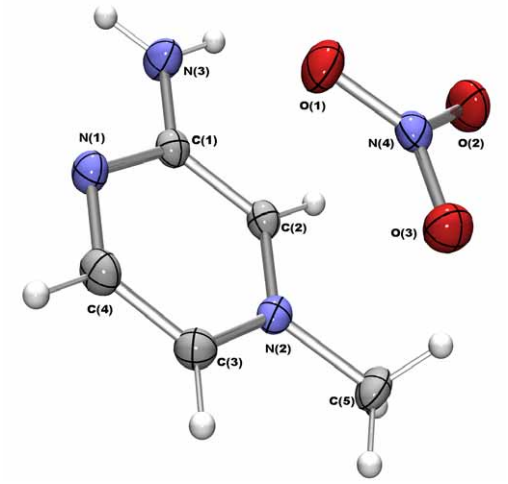

Figure S3: An ORTEP[8] representation of **9**·NO_3, with ellipsoids at the 50% probability level.

The structure of **9**·NO_3 is largely unremarkable, with, as expected, the amino N atom having a trigonal planar geometry (sp^2-hybridisation) owing to its conjugation with the aromatic π-system. Interestingly, however, the distances between the aromatic ring and NO_3^- anion (N(1) containing centroid-O(1) = 3.09 Å, N(2)–N(4) = 3.07 Å) suggest the presence of anion-π interactions.[9] The NO_3^- anions also participate in H-bonding interactions with the amino groups (Table S2), which serve to link the $[Meapyz]^+$ species into a 1-D helical polymer extending along the crystallographic *c*-axis (Fig S4).

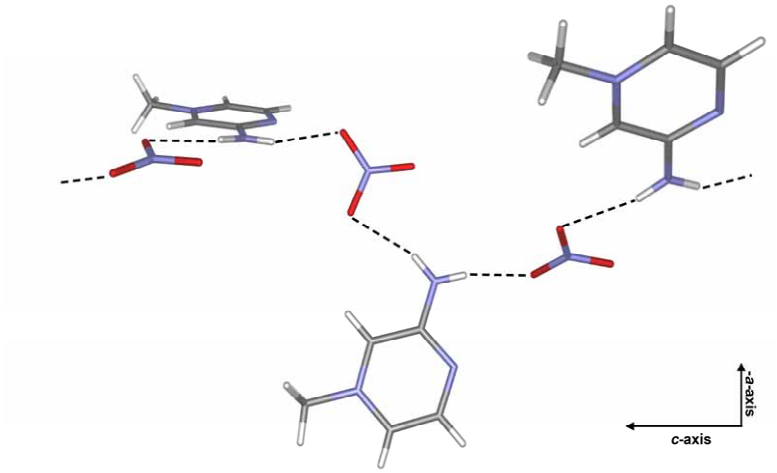

Figure S4: Schematic representation of the H-bonding interactions in the X-ray structure of **9**$^{+}NO_3^{-}$.

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