Supplementary Material (ESI) for Dalton Transactions

SupportingInformation

A neutral Pt_3 stack unsupported by any bridging ligand

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Preparation of **1** and **2**.

Pt(Hpyzpy)Cl_2·H_2O (1a) and Pt(Hpyzpy)Cl_2·$(CH_3)_2CO$ (1b). K_2PtCl_4 (1.26 mmol, 521 mg) and Hpyzpy (0.627 mmol, 91 mg) were dissolved in water (150 mL) and the pH was brought to 3.7 by adding a few drops of 2 M HCl. Within 10 h at room temperature, two fractions (15 and 20 mg) of a yellow solid were filtered off, which contained a mixture of **1a** and *trans*-Pt(pyzpy)$_2$ (**2**), according to ^{1}H NMR spectra (Me_2SO-d_6). The third fraction (142 mg, 53 %) recovered by filtration after 6 d at RT proved to contain exclusively **1a**. Anal.Calcd (%) for $C_8H_9N_3OCl_2Pt$: C, 22.4; H, 2.1; N, 9.8. Found: C, 22.4; H, 2.2; N, 9.5. ^{1}H NMR (δ, ppm, $CDCl_3$): 11.7 (NH,b), 9.60 (dd, 5.6, 1.3 Hz; ^{195}Pt satellites ca 42 Hz; H6), 8.10 (ddd, 7.4, 7.4, 1.3 Hz; H4), 7.02 (d, 2.7 Hz; H5'), 7.77 (dd, 7.4, 1.3 Hz, H3), 7.51 (ddd, 7.4, 5.6, 1.3 Hz; H5), 6.92 (d, 2.7 Hz; H4'). Crude **1a** was dissolved in a minimum amount of DMF and acetone was added. Pale yellow crystals of Pt(Hpyzpy)Cl_2·$(CH_3)_2CO$ (**1b**) were isolated in low yield and characterized by X-ray analysis.

***trans*-Pt(pyzpy)$_2$ (2).** **1** (0.46 mmol, 200 mg) was suspended in water (400 mL), Hpyzpy (1.38 mmol, 200 mg) was added, and the mixture was stirred at 100 °C for 3 d. Yellow **2** was filtered off, washed with water and dried at 40 °C. The yield was 71 % based on **1**. Alternatively, **2** was obtained by refluxing an aqueous mixture of K_2PtCl_4 and Hpyzpy (1:3) for 48 h. Filtration of the yellow precipitate, washing with water and drying in air gave **2** in 77 % yield. Anal.Calcd (%) for $C_{16}H_{12}N_6Pt$: C, 39.8; H, 2.5; N, 17.4. Found: C, 39.6; H, 2.7; N, 17.6. Orange-yellow single crystals suitable for X-ray analysis were obtained upon recrystallization of the crude product from $CHCl_3$.

X-Ray crystallography

Intensity data collections of **1** and **2** were performed on an Enraf–Nonius Kappa CCD (compound **1**) and on an Oxford Diffraction Xcalibur (compound **2**) diffractometers. Data reduction and cell refinement were carried out using the DENZO and SCALE-PACK (for **1**) programs,[1] and CrysAlisPro software (for **2**).[2] All the structures were solved by direct

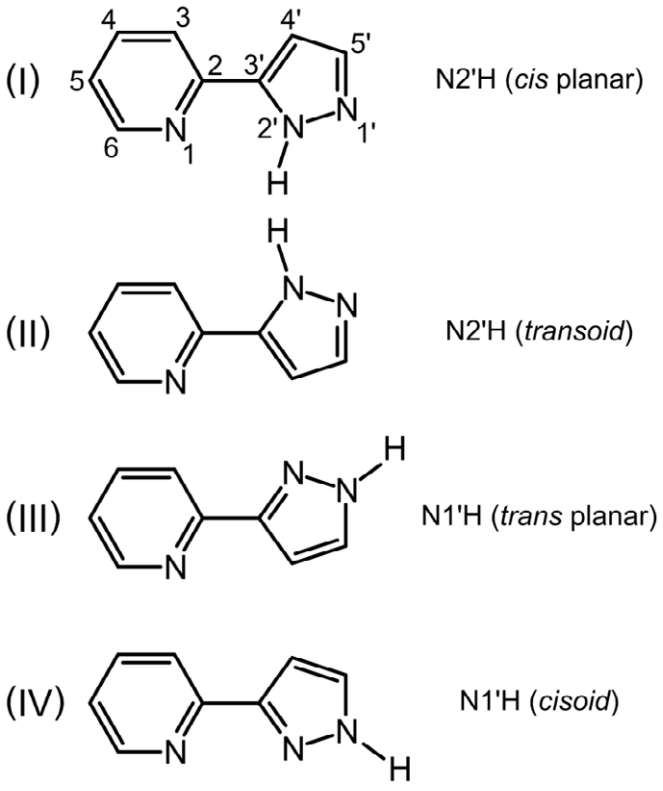
methods and refined by full-matrix least-squares methods based on F^2 using the SHELXL-97 and WinGXprograms.[3,4] All non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were included in geometrically calculated positions and refined with isotropic displacement parameters according to the riding model.

[1] Z. Otwinowsky, W. Minor, "*DENZO and SCALEPACK*". *Methods Enzymol.*1997, **276**, 307.

[2]CrysAlisPro, Oxford Diffraction (Poland), 2009.

[3]G. M. Sheldrick, SHELX97, *"Programs for Crystal Structure Analysis; University of Göttingen"*. Göttingen, Germany, 1998.

[4]L. J. Farrugia, *J. Appl. Crystallogr.*1999, **32**, 837.



Scheme S-1 Hpyzpy in its four most stable tautomeric/rotameric forms: I > II ~ III > IV (according to ref. 2e). Two less stable forms (with proton at N1) are not shown.

Signal	δ / ppm	$J(^1H,^1H)$ / Hz
H6	8.56	5.1
H5	7.54	1.4; 5.3; 7.3
H4	8.09	1.7; 7.4; 8.1
H3	7.98	1.0; 1.2; 8.1
H5'	7.84	2.4
H4'	6.93	2.4

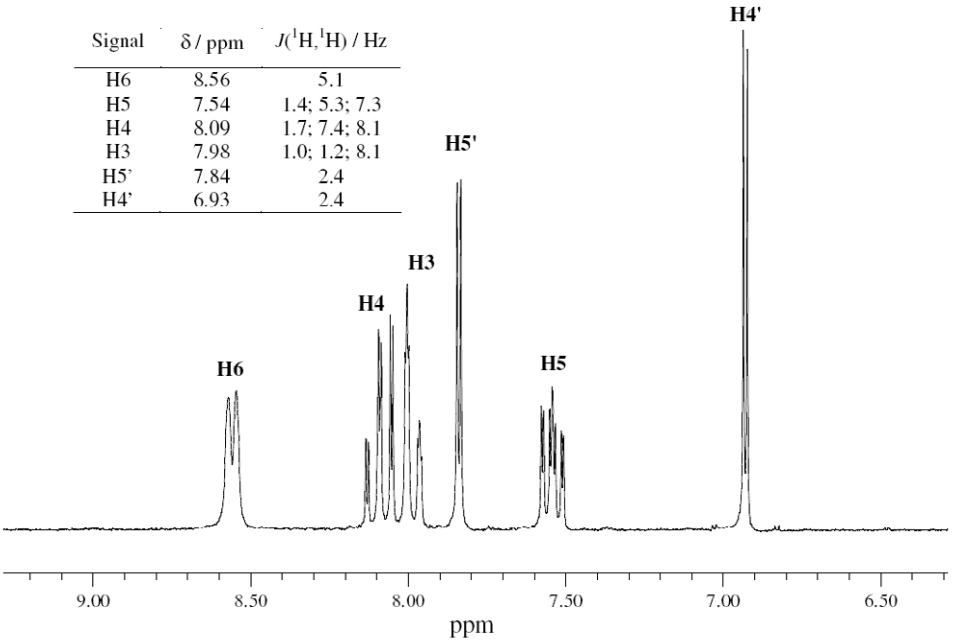


Figure S-1 ^{1}H NMR spectrum of Hpyzpy in D_2O, pD 6.1.

Table S-1 Selected distances (Å) and angles (°) for complex **1**.

Pt1–Cl1	2.284(4)	N2'-Pt1-N1	80.4(5)
Pt1–Cl2	2.287(4)	N2'-Pt1-Cl1	93.3(4)
Pt1–N1	2.017(13)	N1-Pt1-Cl2	94.6(4)
Pt1–N2'	1.989(12)	Cl1-Pt1-Cl2	91.68(16)
		N1-Pt1-Cl1	173.6(4)
		N2'-Pt1-Cl2	174.5(4)

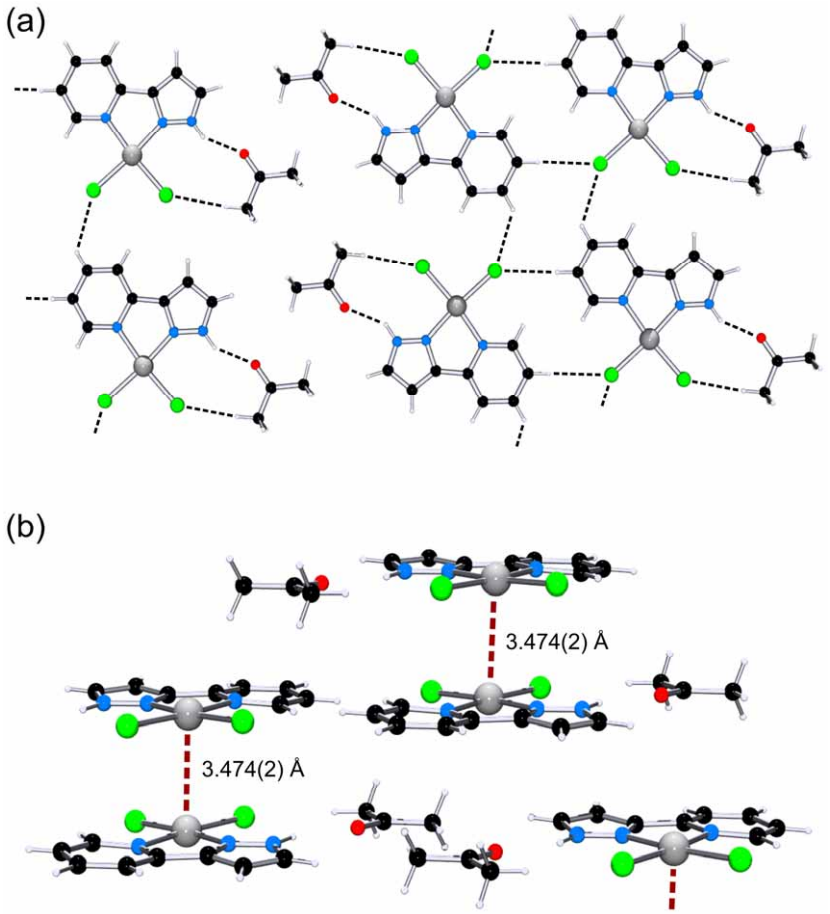
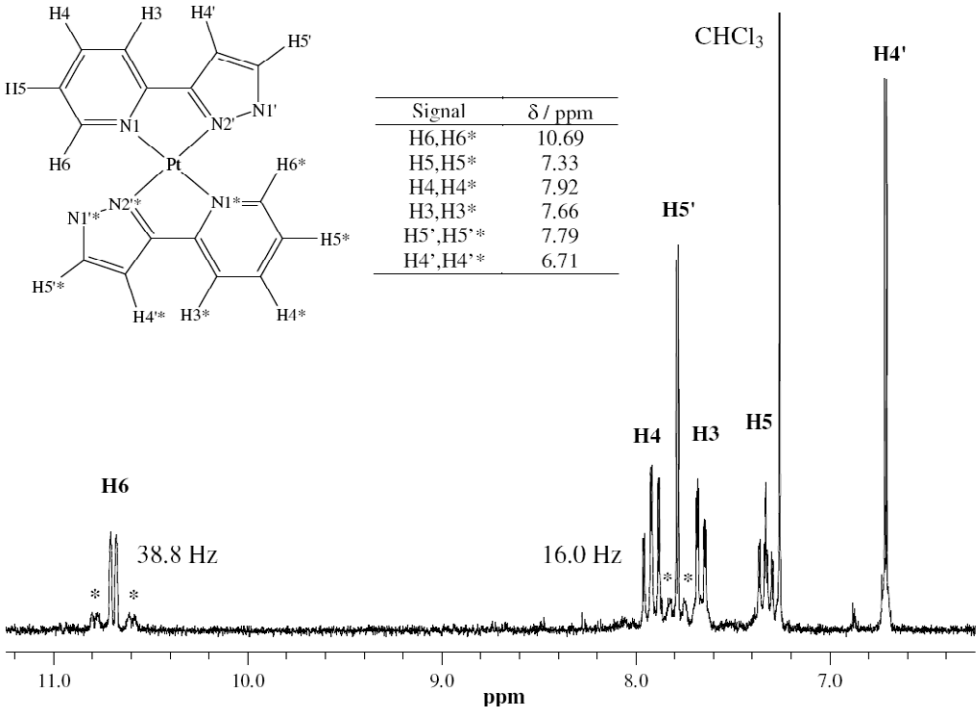


Figure S-2 (a) View of the hydrogen bonding pattern in **1**; (b) Stacking of the Pt(Hpyzpy-*N1*,*N2'*)Cl_2 units, with short Pt···Pt distances.

Table S-2 Selected distances (Å) and angles (°) for complex **2**.

Pt1–N1	2.033(4)	N2'-Pt1-N1	79.41(17)
Pt1–N2'	1.996(4)	N2'-Pt1-N1	100.59(17)
Pt2–N1a	2.033(4)	N1-Pt1-N1	180
Pt2–N1b	2.032(4)	N2'-Pt1-N2'	180
Pt2–N2a'	1.994(4)	N2a'-Pt2-N1a	79.91(16)
Pt2–N2b'	2.001(4)	N2a'-Pt2-N1b	100.07(16)
Pt1···Pt2	3.2985(2)	N2b'-Pt2-N1b	80.05(16)
		N1b-Pt2-N1a	178.60(16)
		N2a'-Pt2-N2b'	176.23(16)



Signal	δ / ppm
H6,H6*	10.69
H5,H5*	7.33
H4,H4*	7.92
H3,H3*	7.66
H5',H5'*	7.79
H4',H4'*	6.71

Figure S-3 ^{1}H NMR spectrum of **2** in $CDCl_3$.