

Cite this: *Dalton Trans.*, 2011, **40**, 5159www.rsc.org/daltonA neutral Pt₃ stack unsupported by any bridging ligand†Lars Holland,^a Wei-Zheng Shen,^a Philipp von Grebe,^a Pablo J. Sanz Miguel,^a Fabio Pichierri,^{*b} Andreas Springer,^c Christoph A. Schalley^c and Bernhard Lippert^{*a}

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Pt...Pt...Pt interactions via their d⁸ orbitals, combined with π-π stacking of deprotonated, chelating 2-(3'-pyrazolyl)pyridine (pyzpy) ligands, are responsible for *trans*-Pt(pyzpy)₂ (**2**) crystallization in a stack of three molecules unsupported by any bridging ligand.

2-(3'-pyrazolyl)pyridine (Hpyzpy) is a *N,N'*-chelating biheteroaromatic ligand with a tradition in coordination chemistry¹ and applied sciences.² It can occur in its neutral form in six possible isomeric forms (tautomers, rotamers; cf. ESI†) and deprotonation to give the monoanion can take place either at N1' or N2' of the pyrazolyl entity. When acting as a chelating ligand for d⁸ metal ions (Pt^{II},^{2b} Pd^{II},³ Au^{III2d}) it is the pyridyl-N1 site and the pyrazolyl-N2' site which are involved. Unlike 2,2'-bpy complexes,⁴ bis-complexes of pyzpy are perfectly planar, which is a consequence of the compared to 2,2'-bpy smaller pyrazole moiety and the possibility to form CH...N hydrogen bonds following deprotonation of the N1'H position. Here we report on two products obtained upon reacting K₂PtCl₄ with Hpyzpy in water (Scheme 1). In both products, Pt(Hpyzpy)Cl₂ (**1**) and *trans* Pt(pyzpy)₂ (**2**), the (H)pyzpy ligands act as chelating ligands via py-N1 and pyz-N2'. **1** was obtained in crystalline form as its acetone solvate (Fig. 1). Molecules of **1** stack in the solid state in pairs (Pt...Pt, 3.474(2) Å), as is not uncommon in Pt^{II} chemistry. There are no unusual structural features with **1** (cf. ESI†).

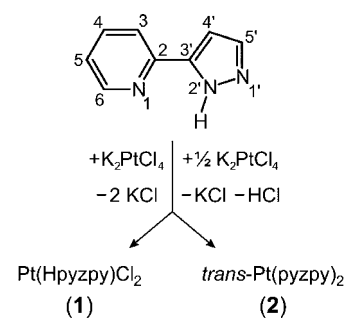
In contrast, **2** is special in that it crystallizes in a rare fashion⁵ in units of three, with the three Pt's stacked right on top of each other. Single crystals of *trans*-Pt(pyzpy)₂ (**2**) were grown from CHCl₃. There are two crystallographically different molecules (**2a**, **2b**) present, which differ slightly. One of these, **2a**, lies on an inversion center, and is shown in Fig. 2 (top). The two chelate rings within a molecule are oriented *trans* to each other.

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† Electronic supplementary information (ESI) available: ¹H NMR spectra of Hpyzpy and **2**, structural details of **1** and **2**, tautomer/rotamer forms of Hpyzpy, details of synthesis of **1** and **2**. CCDC reference numbers 794349 and 794350. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt01408g



Scheme 1 Formation of **1** and **2** from K₂PtCl₄ and Hpyzpy.

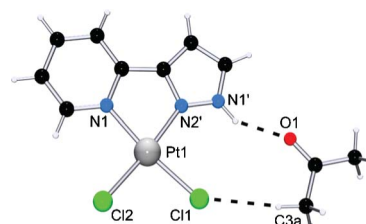


Fig. 1 View of Pt(Hpyzpy-*N1,N2'*)Cl₂·(CH₃)₂CO (**1**) showing the interaction between the Pt complex and the crystallized acetone.

Selected bond lengths and angles are provided in the ESI†. Again, **2a** and **2b** are very similar to that of the corresponding Pd complex.³ This applies also to the short intramolecular hydrogen bonds between the N1' sites of the deprotonated pyrazolylpyridine ligands and the H6 protons of the pyridine entities (N1'-C6 distances are 3.099(7) Å in **2a**, and 3.095(7) Å in **2b**). Unlike **2**, the Pd analogue does not display the unique stacking pattern seen with **2**, however. Compound **2a** undergoes π-stacking with two of the other molecules, **2b**, at either side to produce a trimer stack (Fig. 2, bottom). Within this trimer stack, the two outer molecules (**2b**) are strictly aligned, whereas the inner molecule (**2a**) is flipped and rotated by 22.3°. As a consequence, the two pyzpy rings of **2a** are sandwiched between two pyzpy entities of the two **2b** molecules. Although molecules of **2a** and **2b** are slightly rotated and for this reason the facial superposition of the π-systems is not perfect, this stacking pattern is to be considered rare.⁷ In the large majority of cases of stacking, the π-ligands undergo slippage and overlap to a considerably lesser extent.⁸ It is presumably the Pt...Pt...Pt interactions which enable this specific stacking pattern, similar to the situation with terpyridine ligands in Pt^{II} and Pd^{II} complexes, for example,⁹ or the red form

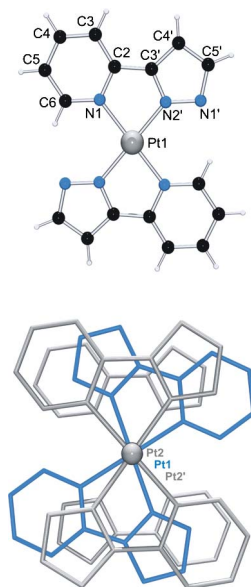


Fig. 2 Top: View of **2a** with atom numbering scheme. Pt1 is situated on an inversion center. H6 is involved in intramolecular hydrogen bonding with N1'. Bottom: View of **2** along the Pt...Pt...Pt axis.

of Pt(2,2'-bpy)Cl₂,¹⁰ or even complex **1**. We note that the closely related *trans*-[Au(pyzzp)₂Cl] complex^{2d} forms dimer stacks in the solid state (3.3 Å) with face-to-face orientation of the chelating ligands, yet with a considerably longer Au...Au separation of 4.5517(5) Å due to slippage. There is another unique feature of the packing pattern of **2**, namely the mutually perpendicular arrangement of trimer stacks (Fig. 3). This packing pattern allows for perpendicular CH...π interactions involving aromatic protons of the pyzpy ligands, with C3b(H)...centroid(N1a'-N2a'), 3.57 Å and C4'(H)...centroid(N1b-C6b), 3.40 Å. This arrangement is eased by the fact that the size of the bis(chelate) of **2** (ca. 10 Å × 10 Å) matches the thickness of the trimeric stack.

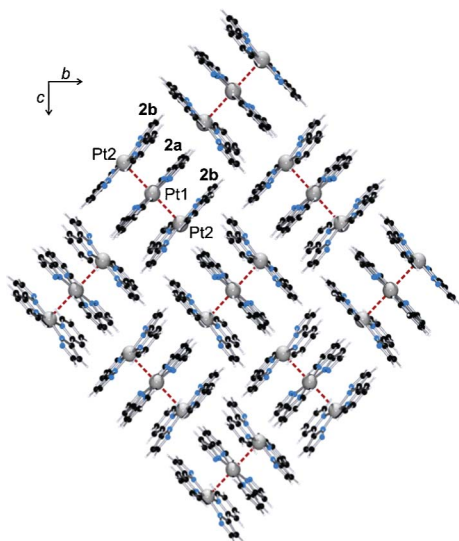


Fig. 3 Upper view (along the *a* axis) of the packing of **2**. The Pt1...Pt2 distance is 3.2985(2) Å.

Details of the ¹H NMR spectra of **1** and **2** are given in the ESI†. The most characteristic resonance of **2** is the strongly downfield

shifted H6 resonance, which displays a doublet (5.7 Hz) at 10.69 ppm and has ³*J*(¹⁹⁵Pt-¹H) satellites of 39 Hz. This large downfield shift of H6 of the anionic ligand as compared to the free ligand (> 2 ppm) and complex **1** with the neutral ligand (1.1 ppm) is due to a combination of Pt^{II} binding to N1 and in particular the hydrogen bonding interaction with the N1' atom in the deprotonated pyrazole entity. Features of the other pyridine resonances H3, H4, H5 (shifts relative to free ligand; coupling patterns) are normal. The two protons of the pyrazolate, H4' and H5', are relatively unaffected as compared to the neutral Hpyzpy ligand. They occur as doublets (³*J*(H4'-H5') 2.1 Hz), and H5' displays ⁴*J*(¹⁹⁵Pt-¹H) coupling of 16 Hz. The ¹⁹⁵Pt chemical shift of **2** in CDCl₃ is -2726 ppm, hence close to Pt^{II} compounds with four N donors in their coordination sphere.¹¹ The ¹H NMR resonances of **2** in CDCl₃ show a moderate concentration dependence, which is consistent with complex stacking. For example, in the concentration range 0.4 × 10⁻³ M–4.8 × 10⁻³ M (factor 12), the H4' resonance shifts to higher field in the most concentrated sample by 0.13 ppm.

Adjusting the ionization parameters to very gentle conditions as described, it was possible to generate mass spectra containing the protonated monomer **2**, [PtL₂+H]⁺, (Fig. 4, top; *m/z*_{exp} 484.088; *m/z*_{calc} 483.085, Δ = 6 ppm). Supporting the findings of the quantum chemical calculations, not just this monomeric species, but also the dimer [Pt₂L₄+H]⁺ (*m/z*_{exp} 967.161, *m/z*_{calc} 967.160, Δ = 1 ppm) as well as ions derived from the trimer have been observed. The [Pt₃L₄-H]⁺ ion (*m/z*_{exp} 1160.105, *m/z*_{calc} 1160.109, Δ = 3 ppm) results from double anion stripping from the trimer of **2**, while [Pt₃L₅]⁺ (*m/z*_{exp} 1305.175, *m/z*_{calc} 1305.174, Δ = 1 ppm) reflects the loss of one anion to generate a charged species detectable by mass spectrometry. The latter one was isolated and fragmented using infrared multiphoton dissociation (IRMPD) experiments, resulting in the loss of PtL₂, and formation of [Pt₂L₃]⁺ (Fig. 4, bottom; *m/z*_{exp} 822.103, *m/z*_{calc} 822.100, 4 ppm). This further supports the thesis of a stacked assembly like shown for the solid phase and derived from quantum chemical calculations (see below).

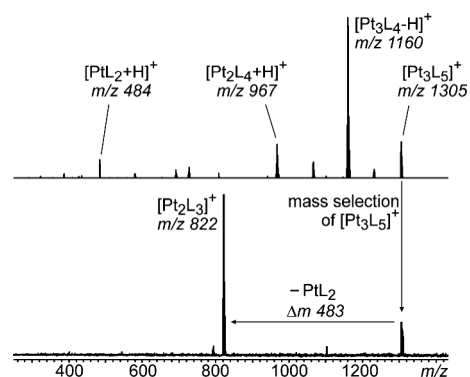


Fig. 4 Top: ESI-FTICR-MS spectrum of **2**. Bottom: Fragmentation of [Pt₃L₅]⁺ in an IRMPD experiment showing the loss of PtL₂.

Stacking interactions between metal complexes of d⁸ metal ions and chelating aromatic ligands are not uncommon, and both di- and polymeric stacks are known. As mentioned, stacks of three metal units are rare.⁵ In order to rationalize why **2** crystallizes as discrete trinuclear entities, quantum chemical calculations¹⁰⁻¹⁵ on small aggregates (dimer, trimer, tetramer) of **2** were carried out. Fig. 5 shows the DFT-optimized geometries of the dimer,

trimer, and tetramer complexes. The Pt...Pt distance in the dimer corresponds to 3.274 Å while the trimer possesses two equivalent Pt...Pt distances of 3.289 Å. This computed value is in excellent agreement with the Pt...Pt distances of 3.2972(7) experimentally observed in the trimer **2**. We also optimized the geometry of the tetramer complex where the fourth Pt monomer unit has the same orientation as the second unit in the stack. Interestingly, the DFT-optimized geometry is characterized by three different Pt...Pt distances, two of which are close to 3.3 Å while the third one is slightly shorter, being at 3.254 Å. Hence, our results indicate that the addition of a fourth Pt unit to the trimer breaks the symmetry in the Pt...Pt distances of the resulting tetramer complex.

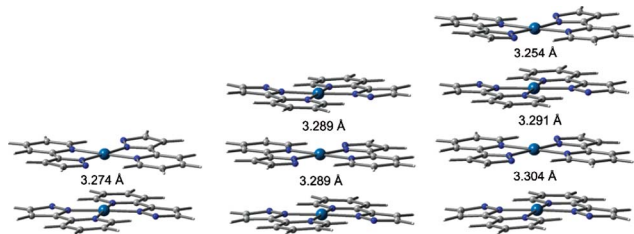


Fig. 5 DFT-optimized structures of the dimer, trimer, and tetramer complexes of *trans*-Pt(pyzy)₂ and Pt...Pt distances.

We have computed the electronic energy associated with the assembly of three units of **2** by taking as reference the total energy of the monomer. The addition of one Pt unit to the dimer complex yields a trimer complex with an energy gain of 12.9 kcal mol⁻¹. When another Pt(pyzy)₂ unit is added to the trimer, the energy gain decreases to 11.3 kcal mol⁻¹, which is smaller than that of 11.7 kcal mol⁻¹ associated with formation of the dimer. This energetic information allows us to propose a rationale on why the infinite stack is not formed in the solid state. As Pt units add up, the resulting n-mer will be stabilized by an amount of energy corresponding to ΔE_n . However, the growth process breaks down when $\Delta E_n < \Delta E_2$. In the case of our neutral *trans*-Pt(pyzy)₂ complex **2**, the growth process stops at n = 3, being $\Delta E_4 < \Delta E_2$. Additional factors, such as optimal packing in the crystal environment together with entropic and kinetic effects, also might play a role, although it is not possible to quantify them with our DFT-based analysis.

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Notes and references

† **1** and **2** were prepared from Hpyzy⁶ and K₂PtCl₄ as described in ESI†. Mass spectra of **2** were generated on a Varian QFT-7 FTICR-MS, equipped with a Cryomagnetix 7T superconducting magnet and a Waters Z-Spray electrospray source. QFT-10x, a peptide standard mixture, was used for external calibration after optimization of all parameters for a maximum abundance of the respective peaks. For the measurements,

the spray voltage was set to 3.8 kV. Other parameters had to be adjusted to very gentle conditions to allow detection without further gas phase reaction. Key parameters which have been optimized were sample cone voltage (45 V), extractor cone voltage (10 V) and especially source- and probe heaters (both 40 °C). The flow rate of freshly prepared solutions of **2** in chloroform (approx. 0.02 mg per mL) was set to 3 μL min⁻¹. For the theoretical values, m/z_{calc} , the ¹⁹⁵Pt isotope was used throughout the experiments and compared with the respective m/z_{exp} . The mass error is presented in ppm.

X-Ray crystallography: Data collection and refinement parameters for **1** and **2** are as follows (further details are given in ESI†).

1: C₁₁H₁₃Cl₂N₃O₂Pt₁, $M = 469.23$, yellow prisms, triclinic, space group $P\bar{1}$, $a = 8.9510(18)$ Å, $b = 8.9970(18)$ Å, $c = 9.6640(19)$ Å, $\alpha = 102.00(3)^\circ$, $\beta = 98.89(3)^\circ$, $\gamma = 108.26(3)^\circ$, $V = 702.4(2)$ Å³, $Z = 2$, $D_c = 2.219$ g cm⁻³, $T = 293(2)$ K, with Mo-K α ($\lambda = 0.71073$), 6032 reflections collected, 2611 unique ($R_{\text{int}} = 0.0963$), $R_1 [I > 2\sigma(I)] = 0.0695$, wR_2 (F, all data) = 0.1497, GoF = 0.996. CCDC 794349.

2: C₁₆H₁₂N₆Pt₃, $M = 483.41$, orange cubes, monoclinic, space group $P2_1/n$, $a = 9.7035(3)$ Å, $b = 13.2662(5)$ Å, $c = 16.4753(5)$ Å, $\beta = 99.019(3)^\circ$, $V = 2094.62(12)$ Å³, $Z = 6$, $D_c = 2.299$ g cm⁻³, $T = 150(2)$ K, with Mo-K α ($\lambda = 0.71073$), 13174 reflections collected, 4842 unique ($R_{\text{int}} = 0.0392$), $R_1 [I > 2\sigma(I)] = 0.0287$, wR_2 (F, all data) = 0.0460, GoF = 0.934. CCDC 794350.

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