

Pyrazine as a Building Block for Molecular Architectures with Pt^{II}Michael Willermann, Clodagh Mulcahy,[†] Roland K. O. Sigel,[‡] Marta Morell Cerdà, Eva Freisinger,[‡] Pablo J. Sanz Miguel, Michael Roitzsch, and Bernhard Lippert*

Fachbereich Chemie, Universität Dortmund, 44221 Dortmund, Germany

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A series of pyrazine (pz) complexes containing *cis*-(NH₃)₂Pt^{II}, (tmeda)Pt^{II} (tmeda = *N,N,N',N'*-tetramethylethylenediamine), and *trans*-(NH₃)₂Pt^{II} entities have been prepared and characterized by X-ray crystallography and/or ¹H NMR spectroscopy. In these compounds, the pz ligands act as monodentate (1–3) or bidentate bridging ligands (4–7). Three variants of the latter case are described: a dinuclear complex [Pt^{II}]₂ (4b), a cyclic tetranuclear [Pt^{II}]₄ complex (5), and a trinuclear mixed-metal complex [Pt₂Ag] (7). Mono- and bidentate binding modes are readily differentiated by ¹H NMR spectroscopy, and the assignment of pz protons in the case of monodentate coordination is aided by the observation of ¹⁹⁵Pt satellites. Formation of the open molecular box *cis*-[{(NH₃)₂Pt(pz)}₄](NO₃)₈·3.67H₂O (5) from *cis*-(NH₃)₂Pt^{II} and pz follows expectations of the “molecular library approach” for the generation of a cyclic tetramer.

Introduction

By now, pyrazine (1,4-diazine, pz) can be considered a “classical” ligand in transition-metal chemistry. To give a few examples, the so-called Creutz–Taube cation [(NH₃)₅-Ru^{II}(pz)Ru^{III}(NH₃)₅]⁵⁺ with the bridging pz ligand was instrumental in understanding intramolecular electron transfer (ET) in mixed-valence-state compounds.¹ Later, pz-bridged metal complexes were applied in order to investigate possible magnetic exchange interactions between dinuclear metal entities.² Even today, ET between pz-bridged Ru₃ clusters is studied in combination with vibrational spectroscopy.³ Closely related to it, solvent dynamics properties are evaluated.⁴ Modification of the basicity of the pz ring as a consequence of coordination of transition-metal fragments

has been another area of topical research,⁵ as has been the fluxional behavior of this ligand.⁶ In recent years, the use of pz as a ditopic donor molecule has become common in the generation of coordination networks and metal-based supramolecular architectures.^{7,8} Finally, pz-bridged dinuclear complexes of Ru and Pt have been prepared and studied with regard to their antitumor activity.⁹

* To whom correspondence should be addressed: E-mail: Bernhard.Lippert@uni-dortmund.de.

[†] Present address: Royal College of Surgeons in Ireland, 123 St. Stephens Green, Dublin 2, Ireland.

[‡] Present address: Institute of Inorganic Chemistry, University of Zürich, 8057 Zürich, Switzerland.

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Our interest in the pz ligand stems from its usefulness as a building block to generate distinct molecular architectures in combination with suitable transition-metal ions. A few examples of such compounds exist, e.g., open Re boxes with luminescence properties,¹⁰ a mixed-valence Creutz–Taube box, [(cyclen)₄Ru₄(pz)₄]⁹⁺,¹¹ a titanocene box,⁷ⁱ and molecular triangles obtained from *cis*-(PMe₃)₂Pt^{II}^{12a} and *cis*-(PPh₃)₂Rh^I.^{12b}

Experimental Section

Materials. *cis*-(NH₃)₂PtCl₂,¹³ (tmeda)PtCl₂¹⁴ (tmeda = *N,N,N',N'*-tetramethylethylenediamine), and *trans*-(NH₃)₂PtCl₂¹⁵ were prepared as reported. Pyrazine (pz) was of a commercial source.

Synthesis of *cis*-[(NH₃)₂Pt(pz)₂](NO₃)₂ (1). *cis*-(NH₃)₂PtCl₂ (203 mg, 0.676 mmol) and AgNO₃ (227.5 mg, 1.339 mmol) were stirred in water (25 mL) in a stoppered flask with daylight excluded for 15 h at 40 °C and then filtered from AgCl. pz (216.7 mg, 2.706 mmol) was added to the clear filtrate and stirred for 3 days at room temperature. The solution was then evaporated to dryness. Under the conditions applied (40 °C, 50 mbar), excess pz is evaporated from the mixture. The residue was then washed with a small amount of water and EtOH to dissolve unreacted Pt starting material. Finally the sample was dried at 50 °C. Yield: 81%. Elem anal. Calcd (%) for C₈H₁₄N₈O₆Pt (513.33): C, 18.7; H, 2.8; N, 21.8. Found: C, 18.6; H, 2.6; N, 21.5. IR (KBr, ν/cm⁻¹): 3435 mb, 3220 s, 3161 s, 1572 m, 1424 s, 1362 vs, 1224 w, 1158 m, 1120 m, 1080 m, 881 w, 808 m, 661 w, 481 m. ¹⁹⁵Pt NMR (D₂O, δ/ppm): -2540. Slow evaporation of a concentrated aqueous solution of **1** yielded colorless crystals suitable for X-ray analysis. The CIF for compound **1** is available from the Cambridge Crystallographic Data Centre (CCDC No. 252454), <http://www.ccdc.cam.ac.uk>.

Synthesis of [(tmeda)Pt(pz)₂](NO₃)₂·H₂O (2). The compound was prepared in analogy to **1**. Yield: 58%. Elem anal. Calcd (%) for C₁₄H₂₆N₈O₇Pt (613.57): C, 27.4; H, 4.3; N, 18.3. Found: C, 27.1; H, 4.1; N, 18.5. IR (KBr, ν/cm⁻¹): 3447 vs, 3095 m, 3004 m, 2922 m, 1637 m, 1384 vs, 1165 m, 1121 m, 1089 m, 824 m.

Synthesis of *trans*-[(NH₃)₂Pt(pz)₂](NO₃)₂ (3). This compound was prepared in analogy to **1** starting from *trans*-(NH₃)₂PtCl₂ and isolated in 85% yield. Elem anal. Calcd (%) for C₈H₁₅N₈O_{6.5}Pt (hemihydrate, 522.34): C, 18.4; H, 2.9; N, 21.5. Found: C, 18.0; H, 2.7; N, 21.5. X-ray crystallography showed the compound to be anhydrous. IR (KBr, ν/cm⁻¹): 3180 s, 3128 s, 3082 s, 3014 m, 1599 m, 1430 s, 1384 vs, 1328 vs, 1163 m, 1080 s, 824 m, 501 m. ¹⁹⁵Pt NMR (D₂O, δ/ppm): -2534.

Synthesis of *cis*-[{(NH₃)₂PtCl₂(pz)]X₂ [X = Cl (4a), ClO₄ (4b)]. *cis*-(NH₃)₂PtCl₂ (500 mg, 1.67 mmol) and pz (63.4 mg, 0.79 mmol) were stirred in water (20 mL) at 40 °C for 3 days. After filtration of some elemental Pt, the solution was concentrated to a volume of 3 mL under a steady flux of N₂. A bright yellow powder (446 mg) was filtered off, washed with ethanol and ether, and dried under vacuum to give **4a**. Yield: 79%. Elem anal. Calcd (%) for C₄H₁₆N₆Cl₄Pt₂ (680.18): C, 7.06; H, 2.37; N, 12.36. Found: C,

6.8; H, 2.3; N, 12.2. IR (KBr, ν/cm⁻¹): 3301 s, 3169 vs, 3099 vs, 3073 vs, 3017 m, 1560 m, 1438 s, 1361 s, 1320 s, 1174 s, 879 m, 835 s, 525 s, 341 m.

Upon the addition of a concentrated aqueous solution of NaClO₄ (10 M, 45 μL) to the filtrate, a yellow microcrystalline material, **4b**, precipitated, which was filtered off, washed with ethanol and ether, and dried in air. **4b** was isolated in 7.9% yield. Elem anal. Calcd (%) for C₄H₁₆N₆O₈Cl₄Pt₂ (808.18): C, 5.94; H, 2.00; N, 10.40. Found: C, 6.3; H, 2.2; N, 10.5. IR (KBr, ν/cm⁻¹): 3302 s, 3218 s, 1636 m, 1559 m, 1433 s, 1339 s, 1312 s, 1084 vs, 832 s, 625 m, 338 m. ¹⁹⁵Pt NMR (D₂O, δ/ppm): -2319.

Synthesis of *cis*-[{(NH₃)₂Pt(pz)}₄](NO₃)₈·3.67H₂O (5). *cis*-(NH₃)₂PtCl₂ (502 mg, 1.67 mmol) was suspended in water (35 mL), and AgNO₃ (563 mg, 3.31 mmol) was added. After 15 h at 40 °C in a stoppered flask and with daylight excluded, AgCl was filtered off and pz (134 mg, 1.67 mmol) was added. After 2 days at 40 °C, the sample was brought to dryness by rotary evaporation (40 °C, 50 mbar), then washed with a small amount of water, and dried at 50 °C. Yield: 53%. The pale-greenish precipitate was then recrystallized from water to give crystals suitable for X-ray analysis. Elem anal. Calcd (%) for C₁₆H_{47.33}N₂₄O_{27.67}Pt₄ (1799.1): C, 10.7; H, 2.7; N, 18.7. Found: C, 10.8; H, 2.6; N, 18.8. IR (KBr, ν/cm⁻¹): 3420 mb, 3210 sb, 3106 s, 3070 s, 1588 m, 1455 s, 1352 vs, 1171 s, 1125 s, 976 w, 819 s, 522 m. ¹⁹⁵Pt NMR (D₂O, δ/ppm): -2535.

Synthesis of [{(tmeda)Pt(pz)}(NO₃)₂·0.75H₂O]_n (n = 3 or 4) (6). An aqueous suspension (15 mL) of (tmeda)PtCl₂ (500 mg, 1.31 mmol) and AgNO₃ (440 mg, 2.59 mmol) was stirred for 24 h at 40 °C with daylight excluded. The resultant AgCl precipitate was filtered off, pz (105 mg, 1.31 mmol) was added to the clear filtrate, and this solution was stirred at room temperature for 24 h. Volume reduction to 5 mL at 40 °C on a rotary evaporator yielded a white precipitate, which was filtered and washed with cold H₂O (5 mL) and dried at 40 °C. Yield: 56%. Elem anal. Calcd (%) for C₁₀H_{21.5}N₆O_{6.75}Pt: C, 22.7; H, 4.1; N, 15.9. Found: C, 22.3; H, 3.9; N, 15.9. IR (KBr, ν/cm⁻¹): 3438 sb, 3088 m, 3004 m, 1637 m, 1426 m, 1386 vs, 1426 s, 1161 m, 1120 m, 1036 m, 994 m, 947 w, 812 m, 750 w, 524 m.

Synthesis of [{(tmeda)Pt(pz)₂}₂Ag](ClO₄)₅·2H₂O (7). Crystals of this compound were grown from an aqueous solution of **2** (0.01 mmol in 2 mL) and AgClO₄ (0.06 mmol) upon cooling (3 °C) for several days. The compound was characterized by X-ray crystallography.

Spectroscopy and Other Measurements. ¹H and ¹⁹⁵Pt NMR spectra were recorded on a Varian Mercury 200 FT NMR instrument with sodium 3-(trimethylsilyl)propanesulfonate (TSP) and Na₂[PtCl₆] used as internal references (δ = 0). The pH (uncorrected pH*) was adjusted by adding NaOD and DNO₃, respectively, to D₂O solutions of the samples and measured by means of a glass electrode. To determine the pK_a of pz by pH-dependent ¹H NMR spectroscopy, uncorrected pH* values were converted into pD values by adding 0.4 to the pH meter reading. pK_a values were evaluated with a Newton–Gauss¹⁶ nonlinear least-squares fit method. The obtained pK_a value for D₂O was then transformed to the value valid for H₂O according to the literature.¹⁷ IR spectra (KBr pellets) were recorded on an IFS 28 FT spectrometer.

X-ray Crystallography. Crystal data (Table 1) for compounds **1**, **3**, **4b**, **5**, and **7** were collected on an Enraf-Nonius-Kappa CCD

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Table 1. Crystallographic Data for Compounds **1**, **3**, **4b**, **5**, and **7**

	1	3	4b	5	7
chemical formula	C ₈ H ₁₄ N ₈ O ₆ Pt	C ₈ H ₁₄ N ₈ O ₆ Pt	C ₄ H ₁₆ Cl ₄ N ₆ O ₈ Pt ₂	C ₁₆ H _{47.33} N ₂₄ O _{27.67} Pt ₄	C ₂₈ H ₄₈ Cl ₅ N ₁₂ O ₂₂ AgPt ₂
fw, g mol ⁻¹	513.36	513.36	808.21	1799.05	1580.08
space group	<i>P2₁/n</i> (No. 14)	<i>P2₁/n</i> (No. 14)	<i>P</i> $\bar{1}$ (No. 2)	<i>C2/c</i> (No. 15)	<i>C2/c</i> (No. 15)
<i>a</i> , Å	5.810(1)	7.860(2)	10.429(2)	22.287(4)	34.927(7)
<i>b</i> , Å	15.870(3)	11.126(2)	10.488(2)	18.922(4)	10.663(2)
<i>c</i> , Å	16.473(3)	8.955(2)	10.575(2)	32.188(6)	13.479(3)
α , deg	90	90	93.30(3)	90	90
β , deg	95.61(3)	103.41(3)	118.70(3)	98.76(3)	98.82(3)
γ , deg	90	90	116.29(3)	90	90
<i>V</i> , Å ³	1511.6(5)	761.7(3)	854.2(3)	13416(4)	4960.6(17)
<i>Z</i>	4	2	2	12	4
<i>T</i> , K	293(2)	293(2)	163(2)	100(2)	120(2)
λ , Å	0.71073	0.71073	0.71073	0.71073	0.71073
<i>D</i> _{calcd} , g cm ⁻³	2.256	2.238	3.142	2.682	2.116
μ , mm ⁻¹	9.329	9.256	17.032	12.592	6.374
final <i>R</i> indices	<i>R</i> 1 = 0.0396, w <i>R</i> 2 = 0.0940	<i>R</i> 1 = 0.0178, w <i>R</i> 2 = 0.0372	<i>R</i> 1 = 0.0208, w <i>R</i> 2 = 0.0510	<i>R</i> 1 = 0.0395, w <i>R</i> 2 = 0.0467	<i>R</i> 1 = 0.0304, w <i>R</i> 2 = 0.0531
[<i>I</i> > 2 σ (<i>I</i>)] ^a	<i>R</i> 1 = 0.0620, w <i>R</i> 2 = 0.0975	<i>R</i> 1 = 0.0395, w <i>R</i> 2 = 0.0397	<i>R</i> 1 = 0.0238, w <i>R</i> 2 = 0.0522	<i>R</i> 1 = 0.1623, w <i>R</i> 2 = 0.0593	<i>R</i> 1 = 0.0534, w <i>R</i> 2 = 0.0593

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

diffractometer¹⁸ using graphite-monochromated Mo K α radiation ($\lambda = 0.7107$ Å). For data reduction and cell refinement, the programs DENZO and SCALEPACK (Nonius, 2000)¹⁹ were used. Absorption corrections based on the multiscan technique were applied for **4b** and **5** using SADABS.²⁰ The structures were solved by conventional Patterson methods and subsequent Fourier syntheses and refined by full-matrix least squares for F^2 using the SHELX program.²¹ The positions of all non-hydrogen atoms were deduced from difference Fourier maps and refined anisotropically. Hydrogen atoms were included in calculated positions and refined with isotropic displacement parameters. In **7**, one of the perchlorate anions (Cl3) is disordered over two positions, with one of the oxygen atoms lying on the 2-fold axis.

Results and Discussion

pz as a Monotopic Ligand. Three compounds, **1**, **2**·H₂O, and **3**, which contain pz as a monotopic ligand, were prepared. X-ray crystal structure analyses were performed for **1** and **3**. The cations of **1** and **3** are depicted in Figures 1 and 2, and salient structural features are listed in the legends. In **1**, the Pt coordination geometry is close to ideal square-planar as far as angles are concerned. Pt–N distances are normal. The pz planes are tilted with respect to the PtN₄ planes with angles of 50.5(2)° (ring a) and 66.2(2)° (ring b). The angle between the two pz rings is 73.6(2)°. There are no unusual features in the pz rings. Expectedly, the internal ring angles at N1 and N4 of the pz ligands are different and larger for the N1 sites carrying the heavy metal. Cations of **1** interact through weak centrosymmetric hydrogen bonds between the noncoordinating ring N atom of pz (N4) and the heteroaromatic protons in the α position (see the Supporting Information). Between a rings, these distances

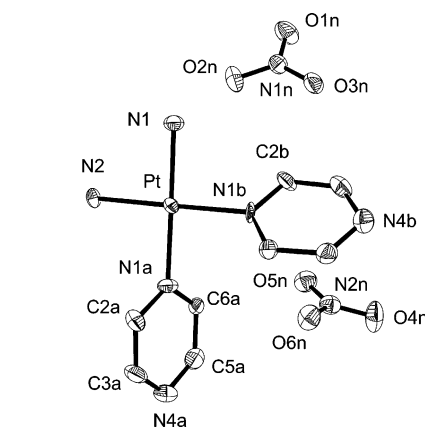


Figure 1. View of **1**. Selected structural details (distances in Å and angles in deg): Pt–N1, 2.048(6); Pt–N2, 2.065(6); Pt–N1a, 2.022(5); Pt–N1b, 2.040(4); N1–Pt–N2, 88.5(3); N1a–Pt–N1b, 89.6(2).

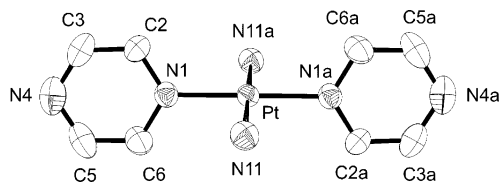


Figure 2. View of **3**. Selected structural details (distances in Å and angles in deg): Pt–N11, 2.011(3); Pt–N1, 2.041(3); N11–Pt–N1, 88.98(12).

are 3.283(9) Å, whereas they are 3.264(8) Å between b rings. Although these distances are relatively long and clearly longer than those in hemiprotonated phenanthroline,²² they can still be considered hydrogen bonds.^{23,24} As a consequence of these interactions, cations of **1** form a zigzag chain along the z axis and Pt centers are lined up along the x axis [5.819(1) Å]. The nitrate anions are located between the zigzag chains and form multiple H bonds to NH₃ groups and long contacts to Pt centers, e.g., 3.581(5) Å between Pt

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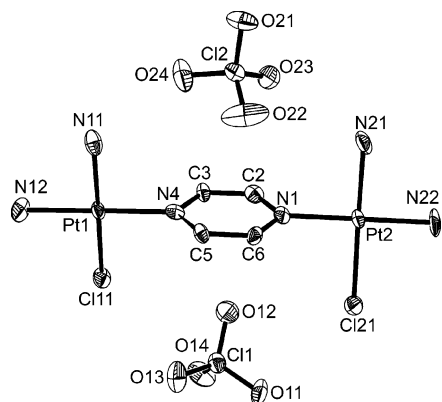


Figure 3. View of **4b**. Selected structural details (distances in Å and angles in deg; see also the text): Pt1–Cl11, 2.292(2); Pt2–Cl21, 2.299(2); N11–Pt1–N12, 88.9(2); N4–Pt1–Cl11, 90.8(1); N21–Pt2–N22, 89.5(2); N1–Pt2–Cl21, 90.5(1).

and O2n ($x + 1, y, z$). The presence of nitrate anions prevents any stacking between pz ligands.

There are no unusual features with the cation of **3**. The pz ligands form angles of $70.9(1)^\circ$ with the PtN₄ plane. Cations form columns extending along the z axis, with distances of 7.7 Å between pz rings. Pairs of nitrate anions are located between the cations and form bifurcated hydrogen bonds with NH₃ ligands of two different cations. In addition, the remaining proton of each NH₃ ligand forms an H bond with the nitrate–O1 of an adjacent column. The lengths of the NH \cdots O bonds vary between 2.953(4) and 3.018(5) Å.

pz as a Bridging Ligand. The reaction of pz with an excess of *cis*-(NH₃)₂PtCl₂ yielded the dinuclear complex **4a**, and subsequent recrystallization in the presence of NaClO₄ gave the corresponding perchlorate salt (**4b**), the structure of which was established by X-ray crystallography. A view of **4b** is given in Figure 3, and selected interatomic distances and angles are listed in the legend. The coordination spheres of the two heavy-metal atoms do not show any peculiarities. Pt–N (pz) distances are identical within standard deviations and on average 2.025(5) Å. The same is true for Pt–NH₃ distances [average 2.039(5) Å]. There is no structural trans influence of the Cl ligands on Pt–NH₃ bond lengths versus the pz ligand. As expected, 2-fold Pt binding leads to identical internal ring angles at N1 [117.4(5) $^\circ$] and N4 [117.7(5) $^\circ$] of the pz ring. The angles between the *cis*-(NH₃)₂Pt^{II} units and the pz plane are different for Pt1 [83.4(3) $^\circ$] and Pt2 [69.3(4) $^\circ$]. As a result, the angle between the two PtN₃Cl planes is 27.4(5) $^\circ$. There is extensive intermolecular hydrogen bonding between pairs of cations involving Cl and NH₃ ligands [N22 \cdots Cl11, 3.530(8) Å; N22 \cdots Cl21, 3.403(6) Å] as well as multiple hydrogen bonds between oxygen atoms of the ClO₄[−] anions and NH₃ groups [distances 2.84(2)–3.39(2) Å]. In the Supporting Information, two views of a pair of cations (with hydrogen-bonded anions omitted for clarity) are provided, which reveal that the two pz rings are parallel, yet do not overlap. The closely related compound *cis*-[{(NH₃)₂PtCl₂(pz)}(NO₃)₂] has been reported before,^{9b} but its cation is centrosymmetric; hence, the Cl ligands are pointing in opposite directions, unlike those in **4b**. Pt–N and Pt–Cl bonds are very similar in the two compounds.

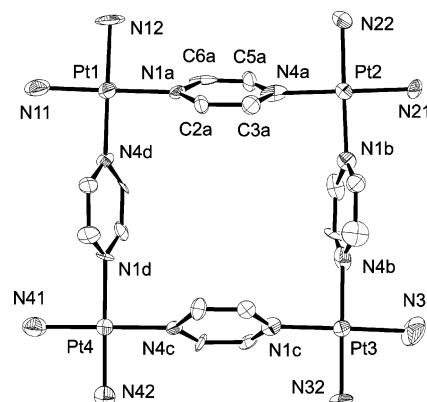


Figure 4. View of the cation of open pz box **5**. Only one of two crystallographically independent cations (**I**) is depicted.

pz Box. Consistent with expectations following the “molecular library approach”,²⁵ a tetranuclear pz box **5** was obtained and isolated upon reacting *cis*-[(NH₃)₂Pt(H₂O)₂]²⁺ and pz in a 1:1 ratio. Formation of **5** was also observed by ¹H NMR spectroscopy in a number of other cases, for example, upon mixing *cis*-[(NH₃)₂Pt(pz)₂]²⁺ and *cis*-[(NH₃)₂Pt(D₂O)₂]²⁺, and identified by its characteristic singlet resonance in the ¹H NMR spectrum (see below). It is interesting to note that Stang and Cao did not observe the formation of a cyclic tetramer when employing (dppp)Pt^{II} [dppp = 1,3-bis(diphenylphosphino)propane²⁶] instead of *cis*-(NH₃)₂Pt^{II}, which the authors attributed to both electronic and steric factors. However, as mentioned in the Introduction, with *cis*-(PMe₃)₂Pt^{II}, a triangular complex can be isolated.^{12a} Compound **5** crystallizes with two independent cations, **I** and **II**. Figure 4 gives a view of one of them (**I**). In **I**, the four metal ions Pt1–Pt4 are essentially coplanar. The pz rings are inclined with respect to the Pt₄ plane as a whole and to individual Pt coordination planes. Dihedral angles (average for two adjacent Pt coordination planes each) are 68.4(3) $^\circ$ for ring a, 78.9(3) $^\circ$ for ring b, 61.2(3) $^\circ$ for ring c, and 69.7(3) $^\circ$ for ring d. We propose to use the term “open box” and not “square” in order to reflect the three-dimensional nature of this object rather than the two-dimensionality generally associated with the term “square”. The latter relates to the arrangement of the four metals only. It also ignores the fact that there are indeed squares with all atoms, hence both the four metals and all atoms of the bridging ligands, being in a plane. Pt \cdots Pt distances along the sides are between 6.79–(1) and 6.81(1) Å, and the separations across the diagonal are 9.59(1) (Pt1 \cdots Pt3) and 9.66(1) Å (Pt2 \cdots Pt4). The second tetranuclear cation (**II**), which is located at a center of inversion, displays rather similar structural details, except for dihedral angles between pz rings and the Pt₄ plane. These are 68.8(3) $^\circ$ for ring f and 89.3(3) $^\circ$ for ring e. The size of the open pz box of **5** thus is slightly smaller than those of the Ru^{II}₃Ru^{III} (6.96 Å)¹¹ and Ti₄ (7.20 Å)⁷ⁱ boxes yet clearly

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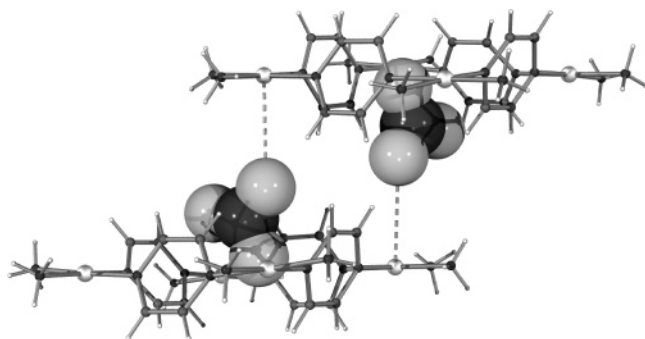


Figure 5. Detail of the interaction of cation **I** of **5** with nitrate anion N30, which is partially inserted in the open pz box. Oxygen atom O33 is pointing toward the center of the box, while O31 makes contact with a Pt from a neighboring cation.

larger than that of the related Pt₄ uracil box,²⁷ in which the Pt–Pt distances along the edges are shorter by almost 1 Å. Pt–NH₃ and Pt–N(pz) bond lengths in **5** are on average 2.04(2) and 2.02(2) Å, respectively, and thus in the normal range. Angles about the Pt atoms deviate by up to 2.1(4)° from 90°, which is likewise normal.

Cations of **5**, nitrate anions, and water molecules (5.5 molecules per 1.5 formula units) form a tight network of hydrogen bonds involving the NH₃ ligands. There are also weak contacts between oxygen atoms of nitrate anions and aromatic pz protons (3.0–3.4 Å). One of the nitrate anions (N30) is unique in that one of its oxygen atoms, O33, is partially inserted in the cavity provided by the four pz rings in cation **I** (Figure 5). It is thus a situation different from that seen in larger cavities of metal hosts.²⁸ The nitrate oxygen atom that protrudes furthest from the box, O31, makes a weak axial contact with a Pt atom [Pt2a, 3.51(1) Å] of an adjacent box. The angle formed between the nitrate anion and the Pt₄ plane is 84.8(4)°. None of the other nitrates behaves analogously.

In analogy to **5**, complex **6** was obtained from (tmeda)Pt^{II} and pz. It is presently unclear whether **6** is indeed a cyclic tetramer or a cyclic trimer only (see below).

Mixed Pt,Ag Polymer. Cocrystallization of **2**·H₂O with AgClO₄ gave **7**. In the cation of **7**, a Ag⁺ ion cross-links the N4 sites of one pz ligand of cation **2** in a linear fashion, with Ag–N4 distances of 2.320(4) Å (Figure 6). These distances are identical with those observed in a related heteronuclear complex of type Co–pz–Ag–pz–Co.²⁹ The overall shape of the cation of **6** is thus that of a Z. The Pt–N1 (pz) distances are normal [average 2.029(4) Å], and the separations between the heavy metals amount to 7.118(1) Å for Pt1···Ag1 and to 14.237(2) Å for Pt1···Pt1* as a result of the centrosymmetry. The most interesting feature of **7** is the way in which individual cations interact (Figure 7). Thus,

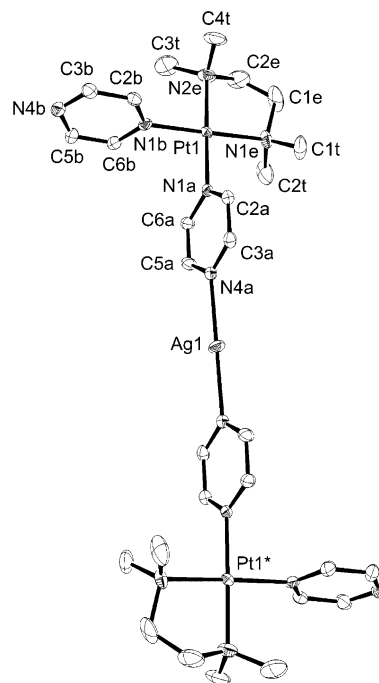


Figure 6. View of centrosymmetric cation **7**.

the N4b sites of the pz ligands form long contacts of 2.586(4) Å with the Ag ions of adjacent cations, which results in the appearance of infinite open Pt₂Ag_{2/2} boxes. The four metals are planar. Angles at the Ag centers are 79.7(1)° and 100.3(1)°, and at the Pt centers, they vary between 85.1(2)° (N1e–Pt1–N2e) and 93.7(2)° (N2e–Pt1–N1b). Within the heteronuclear box intermetallic distances are 9.780(2) Å (Pt1c···Pt1e), 10.663(2) Å (Ag1a···Ag1b), 7.118(1) Å (Pt1a–Ag1a), and 7.349(1) Å (Ag1a···Pt1b).

The polymeric arrangement of the open pz boxes leads to a tape structure with a highly hydrophobic surface generated by the CH groups of the pz ligands as well as the CH₂ and CH₃ groups of the tmeda ligands, which is interrupted by “holes” in the center of the boxes and between the Pt atoms lined up at the periphery of the tape (Figure 7). Piles of such tapes are at a distance of 6.7 Å (between metal planes) and are shifted in such a way that each Ag⁺ of one tape is located above the center of the Pt₂Ag_{2/2} box of the adjacent tape. Similarly, the Pt atoms at the periphery of the tape are on interstitial sites. The repulsion between the positively charged tapes is minimized by perchlorate anions. O41 of ClO₄[−] is inserted into the “hole” within the Pt₂Ag_{2/2} box and, hence, is involved in a host–guest interaction with the cationic box (Figure 8), while one of the other oxygen atoms, O31, forms a weak contact of 2.920(4) Å with the Ag⁺ ion above. Similarly, O22 of ClO₄[−] has a long contact with Pt via an axial position [3.793(4) Å].

The other disordered ClO₄[−] anions (cf. the Experimental Section) are positioned between individual piles.

¹H NMR Spectra. As expected, the ¹H NMR spectrum of free pz consists only of a singlet (8.64 ppm, D₂O, pD 3–9). Below pD ~3, the resonance moves downfield because of protonation of the ring N atoms, with a shift of ~9.2 ppm reached at pD ~0.4. The pK_{a1} value determined from pD-dependent ¹H NMR spectra was 0.9 ± 0.1 (D₂O), which

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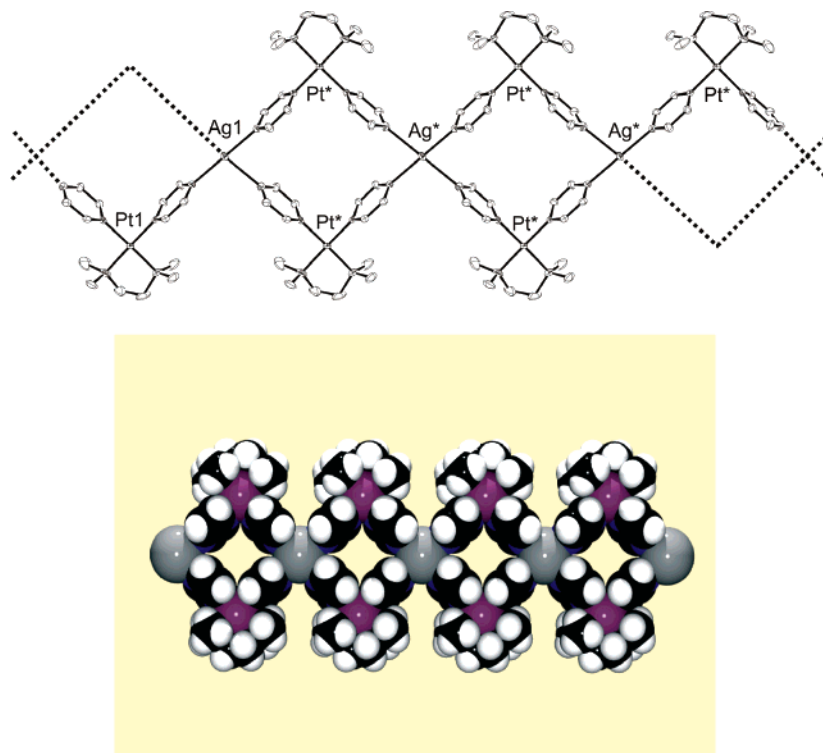


Figure 7. Interactions of Z-shaped cations of **7** to produce an extended structure of open pz boxes. The views are perpendicular to the array of boxes.

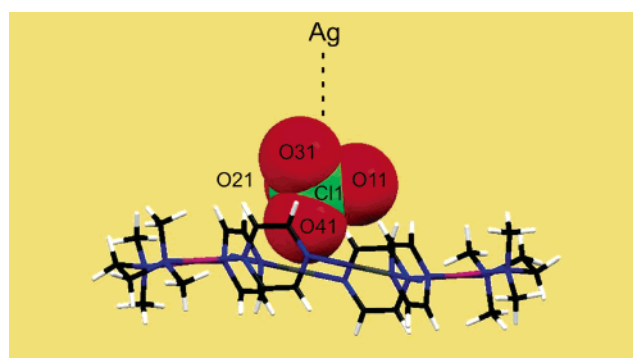


Figure 8. Partial insertion of perchlorate anion ClO_4^- in the $\text{Pt}_2\text{Ag}_{22}$ box. The oxygen atom sticking furthest out of the box (O31) forms a long contact with an Ag^+ ion in the tape above.

corresponds to 0.5 ± 0.1 for water. This value is in good agreement with literature data.³⁰

The ^1H NMR spectra of complexes containing pz bound in a monotopic fashion to Pt^{II} are complex because of ^1H – ^1H coupling in an AA'BB' system. Consequently, the four pz protons in **1**, **2**, and **3** are split into two multiplets because of vicinal and long-range coupling (Figure 9).

Moreover, both sets of resonances display ^{195}Pt coupling of different magnitude, which permits an assignment of the protons. Thus, the set displaying the larger ^{195}Pt coupling constant (3J , ca. 40 Hz) is assigned to H2 and H2' protons in positions ortho to Pt, while the set showing smaller coupling (4J , ca. 11 Hz) is assigned to the protons in meta positions, H3 and H3'.

A comparison of the chemical shifts (center of each multiplet) of the cis and trans isomers **1** and **3** reveals H3

and H3' resonances slightly upfield (ca. 0.1 ppm) in the case of the cis compound, which probably is a consequence of the ring current imposed by the other pz ligand (Table 2).

The ^1H NMR spectrum of **4b** is again very simple, having a sharp singlet at 9.04 ppm (D_2O) and well-resolved ^{195}Pt satellites of 36 Hz. This coupling constant is at the upper end of neutral compounds of composition *trans,trans*- $[\{\text{PtCl}_2(\text{R}_2\text{SO})\}_2(\text{pz})]$, which display 3J values of 28–35 Hz in CDCl_3 .³¹ The open box **5** likewise displays a singlet, which occurs at 9.18 ppm (D_2O , *pD* 4.3) and has two sets of ^{195}Pt satellites due to 4J coupling (5 Hz) and 3J coupling of 32 Hz (Figure 9). The singlet nature of the pz protons of **6** is consistent with a ditopic bridging mode, and the relative intensities of tmeda and pz resonances unambiguously confirm a cyclic structure. We tentatively assign a tetranuclear structure to **6**, although we note that the pz singlet is substantially shifted to lower field (9.497 ppm) as compared to **5**. If the *cis*- $\text{a}_2\text{Pt}(\text{pz})_2$ compounds **1** and **2** are taken as a reference (mean of H2,H2' and H3,H3'), the downfield shift in **5** is 0.16 ppm, yet 0.50 ppm in the case of **6**. This difference may point to a cyclic structure of **6** other than that of a tetramer, e.g., of a trimer. Unfortunately, our attempts to confirm or disprove this suspicion by an X-ray structure analysis or by mass spectrometry were unsuccessful as yet.

Unlike in pz complexes carrying *trans*- PtCl_2L entities with L = phosphine or ethylene,³² in the compounds described herein, no dynamic processes were observed in solution.

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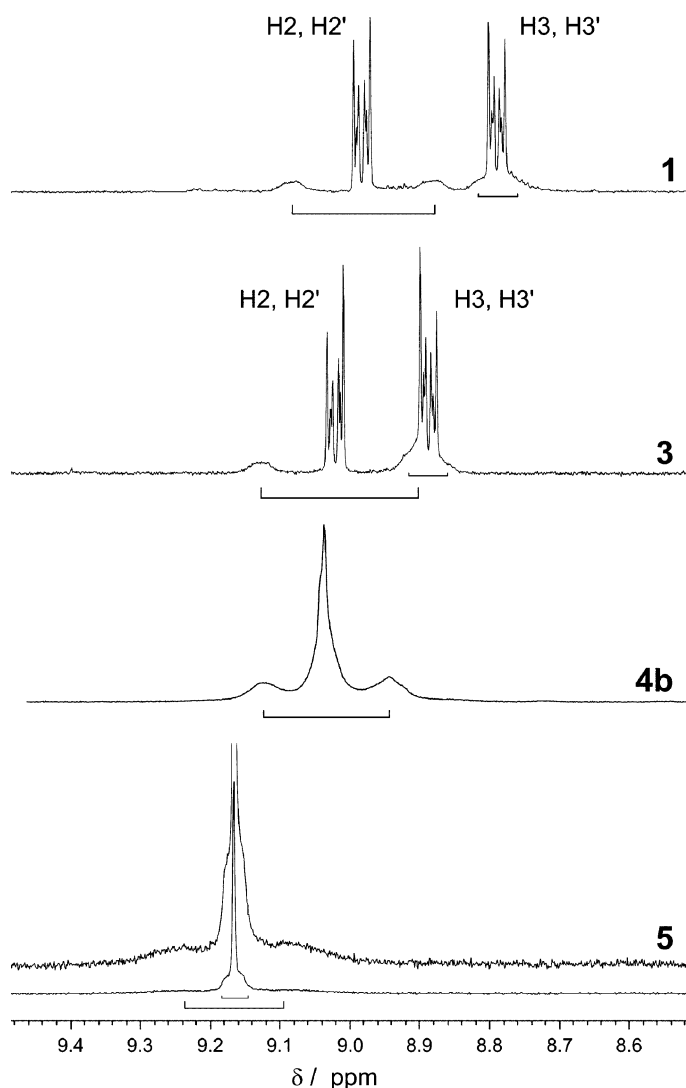


Figure 9. Aromatic regions of ^1H NMR spectra (D_2O) of **1** (pD 5.9), **3** (pD 3), **4b** (pD 5), and **5** (pD 4.3). ^{195}Pt satellites are pointed out.

Table 2. ^1H NMR Data of pz Complexes in D_2O (pD 3–5)

compd	$\delta(\text{H2,H2}'),^a$ $J(^{195}\text{Pt}-^1\text{H})^{b,c}$	$\delta(\text{H3,H3}'),^a$ $J(^{195}\text{Pt}-^1\text{H})^{b,d}$	$\delta(\text{CH}_2),$ $J(^{195}\text{Pt}-^1\text{H})^{b,c}$	$\delta(\text{CH}_3),$ $J(^{195}\text{Pt}-^1\text{H})^{b,c}$
1	8.968, 39	8.778, 12		
2	9.154, 39	8.835, 11	3.151, 26.4	2.818, 33.6
3	9.004, 42	8.873, 11		
4b	9.036, 36 ^{b,c}			
5	9.170, 32 ^{b,c} 5 ^{b,d}			
6	9.497 ^e		3.107 ^e	2.697 ^e

^a In ppm; center of the multiplet. ^b In Hz. ^c 3J coupling. ^d 4J coupling. ^e ^{195}Pt satellites not observed.

Preliminary NMR studies indicate that the pz box **5** is remarkably inert toward nucleobases when kept in an aqueous solution.

Compound 5 and Anions. Considering the solid-state structure of **5** (Figure 5) and following up on an earlier finding that cationic Pt containing cycles with heterocyclic ligands can act as anion receptors,^{28a,33} ^1H NMR spectroscopy of **5** in D_2O in the presence of increasing amounts of alkali salts (H_2PO_4^- , SO_4^{2-} , and F^-) was performed. However, they did not provide any indication of anion binding in water considering the insensitivity of the pz resonance of **5**.

Related pz Compounds. In addition to the pz complexes described above, we have observed the formation of related compounds in solution in a number of cases. The identification of compounds was straightforward on the basis of ^1H NMR spectroscopy. For example, $[\text{enPt}(\text{pz})_2]^{2+}$ is identified by its pz multiplets centered at 8.94 ppm [$^3J(^{195}\text{Pt}-^1\text{H})$, 37 Hz] and 8.00 ppm [$^3J(^{195}\text{Pt}-^1\text{H})$, 9 Hz] and its CH_2 resonance at 2.85 ppm [$^3J(^{195}\text{Pt}-^1\text{H})$, 44 Hz]. $[\text{enPd}(\text{pz})_2]^{2+}$ has its pz multiplets at 8.94 and 8.84 ppm and the CH_2 resonance of the en ligand at 2.94 ppm.

Summary

The compounds prepared in this work confirm the good ligating properties of pz for Pt^{II} , which is somewhat unexpected considering the low basicity of the pz ligand itself. Both complexes with monotopic and ditopic (bridging) metal-binding patterns have been isolated. The formation of the cyclic tetramer **5** conforms to expectations of the “molecular library approach”, which predicts a molecular box when two ditopic building blocks with 90° and 180° angles, respectively, are combined.

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Supporting Information Available: Hydrogen-bonding pattern of **1**, views of a pair of cations of **4b**, and X-ray crystallographic files, in CIF format, for compounds **3**, **4b**, **5**, and **7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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