Pyrazine as a building block for molecular architectures with PtII

Willermann, M ; Mulcahy, C ; Sigel, Roland K O ; Cerdà, M M ; Freisinger, Eva ; Sanz Miguel, P J ; Roitzsch, M ; Lippert, B

Abstract: A series of pyrazine (pz) complexes containing cis-(NH(3))(2)Pt(II), (tmeda)Pt(II) (tmeda = N,N,N',N'-tetramethylethylenediamine), and trans-(NH(3))(2)Pt(II) entities have been prepared and characterized by X-ray crystallography and/or (1)H 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 [Pt(2)Ag] (7). Mono- and bidentate binding modes are readily differentiated by (1)H NMR spectroscopy, and the assignment of pz protons in the case of monodentate coordination is aided by the observation of (195)Pt satellites. Formation of the open molecular box cis-[(NH(3))(2)Pt(pz)(4)](NO(3))(8).3.67H(2)O (5) from cis-(NH(3))(2)Pt(II) and pz follows expectations of the "molecular library approach" for the generation of a cyclic tetramer.

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

Received ……………………………

Abstract

A series of pyrazine (pz) complexes containing *cis*-$(NH_3)_2Pt^{II}$, (tmeda)Pt^{II}, and *trans*-$(NH_3)_2Pt^{II}$ 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 $[Pt_2Ag]$ (**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 ^{195}Pt satellites. Formation of the open molecular box *cis*-$[\{(NH_3)_2Pt(pz)\}_4](NO_3)_8 \cdot 3.67H_2O$ (**5**) from *cis*-$(NH_3)_2Pt^{II}$ and pz follows expectations of the "molecular library approach" for the generation of a cyclic tetramer.

*   Author 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.

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 $[(NH_3)_5Ru^{II}(pz)Ru^{III}(NH_3)_5]^{5+}$ with the bridging pyrazine 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 pyrazine-bridged Ru_3 clusters is studied in combination with vibrational spectroscopy.[3] Closely related to it, solvent dynamics properties are evaluated.[4] Modifications of the basicity of the pyrazine 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 pyrazine as a ditopic donor molecule has become common in the generation of coordination networks and metal-based supramolecular architectures.[7,8] Finally, pyrazine-bridged dinuclear complexes of Ru and Pt have been prepared and studied with regard to their antitumor activity.[9]

Our interest in the pyrazine 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 square, $[(cyclen)_4Ru_4(pz)_4]^{9+}$,[11] a titanocene box,[7i] and molecular triangles obtained from *cis*-$(PMe_3)_2Pt^{II}$ [12a] and *cis*-$(PPh_3)_2Rh^{I}$.[12b]

Experimental Section

Materials. *Cis*-$(NH_3)_2PtCl_2$,[13] $(tmeda)PtCl_2$ [14] (tmeda = *N,N,N',N'*-tetramethyl-ethylenediamine) and *trans*-$(NH_3)_2PtCl_2$ [14] were prepared as reported. Pyrazine (pz) was of a commercial source.

Synthesis of *cis*-[(NH$_3$)$_2$Pt(pz)$_2$](NO$_3$)$_2$ (1). *Cis*-$(NH_3)_2PtCl_2$ (203 mg, 0.676 mmol) and $AgNO_3$ (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. Pyrazine (216.7 mg, 2.706

mmol) was added to the clear filtrate and stirred for 3 d 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 %. Elemental analysis calcd (%) for $C_8H_{14}N_8O_6Pt$ (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. ^{195}Pt NMR (D_2O, δ/ppm) -2540. Slow evaporation of a concentrated aqueous solution of **1** yielded colorless crystals suitable for X-ray analysis.

Synthesis of [(tmeda)Pt(pz)$_2$](NO$_3$)$_2$·H$_2$O (2). The compound was prepared in analogy to **1**. The yield was 58 %. Elemental analysis calcd (%) for $C_{14}H_{26}N_8O_7Pt$ (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*-[(NH$_3$)$_2$Pt(pz)$_2$](NO$_3$)$_2$ (3). This compound was prepared in analogy to **1** and isolated in 85 % yield. Elemental analysis calcd (%) for $C_8H_{15}N_8O_{6.5}Pt$ (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. ^{195}Pt NMR (D_2O, δ/ppm) -2534.

Synthesis of *cis*-[{(NH$_3$)$_2$PtCl}$_2$(pz)]X$_2$ (X = Cl (4a), ClO$_4$ (4b)). *cis*-(NH$_3$)$_2$PtCl$_2$ (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 N_2. A bright yellow powder (446 mg) was filtered off, washed with ethanol and ether and dried under vacuum to give **4a**. The yield was 79 %. Elemental analysis calcd (%) for $C_4H_{16}N_6Cl_4Pt_2$ (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 addition of a concentrated aqueous solution of NaClO$_4$ (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. Elemental analysis calcd (%) for $C_4H_{16}N_6O_8Cl_4Pt_2$ (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. ^{195}Pt NMR (D_2O, δ/ppm) -2319.

Synthesis of *cis*-[{(NH$_3$)$_2$Pt(pz)}$_4$](NO$_3$)$_8$·3.67H$_2$O (5). *cis*-(NH$_3$)$_2$PtCl$_2$ (502 mg, 1.67 mmol) was suspended in water (35 mL) and AgNO$_3$ (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 d 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. Elemental analysis calcd (%) for $C_{16}H_{47.33}N_{24}O_{27.67}Pt_4$ (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. ^{195}Pt NMR (D_2O, δ/ppm) -2535.

Synthesis of [{(tmeda)Pt(pz)}(NO$_3$)$_2$·0.75H$_2$O]$_n$ (n = 3 or 4) (6). An aqueous suspension (15 mL) of (tmeda)PtCl$_2$ (500 mg, 1.31 mmol) and AgNO$_3$ (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 H$_2$O (5 mL) and dried at 40°C. Yield 56 %. Elemental analysis calcd (%) for $C_{10}H_{21.5}N_6O_{6.75}Pt$: 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)$_2$}$_2$Ag](ClO$_4$)$_5$·2H$_2$O (7). Crystals of this compound were grown from an aqueous solution of **2** (0.01 mmol in 2 mL) and AgClO$_4$ (0.06 mmol) upon cooling (3 °C) for several days. The compound was characterized by X-ray crystallography.

Spectroscopy and Other Measurements. ^{1}H NMR and [195]Pt NMR spectra were recorded on a Varian Mercury 200 FT NMR instrument with TSP (sodium 3-trimethylsilyl-propanesulfonate) and $Na_2[PtCl_6]$ used as internal references ($\delta = 0$). The pH (uncorrected pH[*]) was adjusted by adding NaOD and DNO_3, respectively, to D_2O solutions of the samples and measured by means of a glass electrode. In order to determine the pK_a of pz by pH dependent ^{1}H 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-Gauss[16] nonlinear least-squares fit method. The obtained pK_a value for D_2O was then transformed to the value valid for H_2O according to the literature.[17] IR spectra (KBr pellets) were recorded on an IFS 28 FT spectrometer.

X-ray Crystallography. Crystal data for compounds **1**, **3**, **4b**, **5**, and **7** were collected on an Enraf-Nonius-KappaCCD diffractometer[18] using graphite-monochromated MoKα 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 (Cl(3)) is disordered over two positions, with one of the oxygen atoms lying on the twofold axis.

Results and Discussion

Pyrazine as a Monodentate Ligand. Three compounds, *cis*-[(NH$_3$)$_2$Pt(pz)$_2$] (NO$_3$)$_2$·H$_2$O (**1**), [(tmeda)Pt(pz)$_2$](NO$_3$)$_2$·H$_2$O (**2**), and *trans*-[(NH$_3$)$_2$Pt(pz)$_2$](NO$_3$)$_2$ (**3**), which contain pyrazine as monodentate ligands, 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 legend. 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 toward the PtN$_4$ 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 non-coordinating ring-nitrogen atom of pyrazine (N4) and the heteroaromatic protons in the α-position (Figure 3). Between a-rings these distances 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 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 NH$_3$ groups and long contacts to Pt centers, e.g. 3.581(5) Å between Pt 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 *trans*-[(NH$_3$)$_2$Pt(pz)$_2$](NO$_3$)$_2$ (**3**). The pz ligands form angles of 70.9(1)° with the PtN$_4$ 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 NH$_3$ ligands of two different cations. In addition, the remaining proton of each NH$_3$ ligand forms a H bond with nitrate-O1 of an adjacent column. The lengths of the NH…O bonds vary between 2.953(4) and 3.018(5) Å.

Pyrazine as a Bridging Ligand. The reaction of pyrazine with an excess of *cis*-(NH$_3$)$_2$PtCl$_2$ yielded the dinuclear complex *cis*-[{(NH$_3$)$_2$PtCl}$_2$(pz)]Cl$_2$ (**4a**) and subsequent recrystallization in the presence of NaClO$_4$ gave the corresponding perchlorate salt (**4b**), the structure of which was established by X-ray crystallography. A view of **4b** is given in Figure 4 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-NH$_3$ distances (av. 2.039(5) Å). There is no structural *trans*-influence of the Cl ligands on Pt-NH$_3$ bond lengths vs. the pz ligand. As expected, twofold Pt binding leads to identical internal ring angles at N1 (117.4(5)°) and N4 (117.7(5)°) of the pz ring. The angles between the *cis*-(NH$_3$)$_2$Pt^{II} units and the pz plane are different for Pt1 (83.4(3)°) and Pt2 (69.3(4)°). As a result, the angle between the two PtN$_3$Cl planes is 27.4(5)°. There is extensive intermolecular

hydrogen bonding between pairs of cations involving Cl and NH_3 ligands (N(22)…Cl(11), 3.530(8) Å; N(22)…Cl(21), 3.403(6) Å) as well as multiple hydrogen bonds between oxygen atoms of the ClO_4^- anions and NH_3 groups (distances 2.84(2) - 3.39(2) Å). Figure 5 provides two views of a pair of cations (with hydrogen bonded anions omitted for clarity) which reveal that the two pz rings are parallel, yet do not overlap. The closely related compound *cis*-[{(NH_3)_2PtCl}_2(pz)](NO_3)_2$ has been reported before,[9b] but its cation is centrosymmetric, hence the Cl ligands are pointing into opposite directions, unlike in **4b**. Pt-N and Pt-Cl bonds are very similar in the two compounds.

A Pyrazine Box. Consistent with expectations following the "molecular library approach",[25] a tetranuclear pyrazine box *cis*-[{(NH_3)_2Pt(pz)}_4](NO_3)_8·3.67H_2O (**5**) was obtained and isolated upon reacting *cis*-[(NH_3)_2Pt(H_2O)_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*-[(NH_3)_2Pt(pz)_2]^{2+}$ and *cis*-[(NH_3)_2Pt(D_2O)_2]^{2+}$, and identified by its characteristic singlet resonance in the ^1H NMR spectrum (see below). It is interesting to note that Stang and Cao did not observe formation of a cyclic tetramer when employing (dppp)Pt^{II} (dppp = 1,3-bis(diphenylphosphino)propane[26]) instead of *cis*-(NH_3)_2Pt^{II}$, which the authors attributed to both electronic and steric factors. However, as mentioned in the introduction, with *cis*-(PMe_3)_2Pt^{II}$ a triangular complex can be isolated.[12a] Compound **5** crystallizes with two independent cations, (I) and (II). Figures 6 gives a view of one of it (I). In (I) the four metal ions Pt1-Pt4 are essentially coplanar. The pyrazine rings are inclined with respect to the Pt_4 plane. Dihedral angles (av. for two adjacent Pt coordination planes each) are 68.4(3)° for ring "a", 78.9(3)° for ring "b", 61.2(3)° for ring "c", and 69.7(3)° for ring "d". Pt…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…Pt3) and 9.66(1) Å (Pt2…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 Pt_4 plane. These are 68.8(3)° for rings "f" and 89.3(3)° for rings "e". The size of the open pyrazine boxes of **5** thus is slightly smaller than that of the $Ru^{II}_3Ru^{III}$ (6.96 Å)[11] and Ti_4 (7.20 Å)[7i] boxes, yet clearly larger than that of the related Pt_4 uracil box,[27] in which the Pt-Pt distances along the edges are shorter by almost 1 Å. $Pt-NH_3$ 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 NH_3 ligands. There are also weak contacts between oxygen atoms of nitrate anions and aromatic pyrazine 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 7). It is thus a situation different from that seen in larger cavities of metal hosts.[28] The nitrate oxygen atom which 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 pyrazine. It is presently unclear whether **6** is indeed a cyclic tetramer or a cyclic trimer only (see below).

A Mixed Pt,Ag Polymer. Cocrystallization of $[(tmeda)Pt(pz)_2](NO_3)_2 \cdot H_2O$ (**2**) with $AgClO_4$ gave $[\{(tmeda)Pt(pz)_2\}_2Ag](ClO_4)_5 \cdot 2H_2O$ (**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 8). 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 (av. 2.029(4) Å), and the separations between the heavy metals amount to 7.118(1) Å for Pt(1)…Ag(1), and to 14.237(2) Å for Pt(1)…Pt(1a) due to the centrosymmetry. The most interesting feature of **7** is the way in which individual cations interact (Figure 9). Thus, the N(4c) 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 $Pt_2Ag_{2/2}$ 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)° (N(1e)-Pt(1)-N(2e)) and 93.7(2)° (N(2e)-Pt(1)-N(1b)). Within the heteronuclear box intermetallic distances are 9.780(2) Å (Pt(1c)…Pt(1e)), 10.663(2) Å (Ag(1a)…Ag(1b)), 7.118(1) Å (Pt(1a)-Ag(1a)), and 7.349(1) Å (Ag(1a)…Pt(1b)).

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 CH_2 and CH_3 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 9). Piles of such tapes are at a distance of 6.7 Å (between metal planes) and shifted in such a way that each Ag^+ of one tape is located above the center of the $Pt_2Ag_{2/2}$ 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. O(41) of Cl(1)O$_4^-$ is inserted into the "hole" within the Pt$_2$Ag$_{2/2}$ box, hence is involved in a host-guest interaction with the cationic box (Figure 10), while one of the other oxygen atoms, O(31), forms a weak contact of 2.920(4) Å to the Ag$^+$ ion above. Similarly, O(22) of Cl(2)O$_4^-$ has a long contact with Pt via an axial position (3.793(4) Å).

The disordered ClO$_4^-$ anions (c.f. Experimental) are positioned between individual piles.

^{1}H NMR Spectra. As expected, the ^{1}H NMR spectrum of free pz consists only of a singlet (8.64 ppm; D$_2$O; pD 3-9). Below pD ~ 3 the resonance moves downfield due to 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 ^{1}H NMR spectra was 0.9 ± 0.1 (D$_2$O), which corresponds to 0.5 ± 0.1 for water. This value is in good agreement with literature data.[30]

The ^{1}H NMR spectra of complexes containing pz bound in a monodentate fashion to Pt^{II} are complex due to ^{1}H,^{1}H coupling in a AA'BB' system. Consequently the four pz protons in **1**, **2**, and **3** are split into two multiplets due to vicinal and long range coupling (Figure 11).

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 *ortho* positions 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 chemical shifts (center of each mutiplet) of *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 ^{1}H NMR spectrum of **4b** is again very simple, having a sharp singlet at 9.04 ppm (D$_2$O) and well resolved ^{195}Pt satellites of 36 Hz. This coupling constant is at the upper end of neutral compounds of composition *trans*,*trans*-[{PtCl$_2$(R$_2$SO)}$_2$(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$_2$O, pD 4.3) and has two sets of ^{195}Pt satellites due to ^4J coupling (5 Hz) and ^3J coupling of 32 Hz (Figure 10). The singlet nature of the pz protons of **6** is consistent with a bridging mode,

and 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*-a$_2$Pt(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 pyrazine complexes carrying *trans*-PtCl$_2$L entities with L = phosphine or ethylene,[32] in the compounds described herein no dynamic processes were observed in solution. Preliminary NMR studies indicate that the pz box **5** is remarkably inert toward nucleobases when kept in aqueous solution.

Compound 5 and Anions. Considering the solid state structure of **5** (Figure 7) and following up on an earlier finding that cationic Pt containing cycles with heterocyclic ligands can act as anion receptors,[28a,33] ^{1}H NMR spectra of **5** in D$_2$O in the presence of increasing amounts of alkali salts (H$_2$PO$_4^-$, SO$_4^{2-}$, F$^-$) were performed. However, they did not provide any indication of anion binding in water considering the insensitivity of the pz resonance of **5**.

Related Pyrazine Compounds. In addition to the pz complexes described above, we have observed formation of related compounds in solution in a number of cases. The identification of compounds was straightforward on the basis of ^{1}H NMR spectroscopy. For example, [enPt(pz)$_2$]$^{2+}$ is identified by its pz multiplets centered at 8.94 ppm ($^3J(^{195}$Pt-^{1}H), 37 Hz) and 8.00 ppm ($^3J(^{195}$Pt-^{1}H), 9 Hz) and its CH$_2$ resonance at 2.85 ppm ($^3J(^{195}$Pt-^{1}H), 44 Hz). [enPd(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 pyrazine for Pt^{II}, which is somewhat unexpected considering the low basicity of the pz ligand itself. Both complexes with monodentate and bidentate bridging metal binding patterns have been

isolated. 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.

Supporting Information Available: X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org for compounds **3**, **4b**, **5** and **7**. The CIF for compound **1** is available from the Cambridge Crystallographic Data Centre (CCDC No. 252454), http://www.ccdc.cam.ac.uk.

References

(1)   (a) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1. (b) Taube, H. *Angew. Chem. Int. Edit.* **1984**, *23*, 329.

(2)   See, e.g.: Cotton, F. A.; Kim, Y.; Ren, T. *Inorg. Chem.* **1992**, *31*, 2608.

(3)   (a) Ito, T.; Hamaguchi, T.; Nagino, H.; Yamaguchi, T.; Washington, J.; Kubiak, C. P. *Science* **1997**, *277*, 660. (b) Ito, T.; Hamaguchi, T.; Nagino, H.; Yamaguchi, T.; Kido, H.; Zavarine, I. S.; Richmond, T.; Washington, J.; Kubiak, C. P. *J. Am. Chem. Soc.* **1999**, *121*, 4625.

(4)   (a) Londergan, C. H.; Salsman, J. C.; Ronco, S.; Dolkas, L. M.; Kubiak, C. P. *J. Am. Chem. Soc.* **2002**, *124*, 6236. (b) Londergan, C. H.; Kubiak, C. P. *Chem. Eur. J.* **2003**, *9*, 5962.

(5)   See, e.g.: (a) Ford, P.; Rudd, D. P.; Gaunder, R.; Taube H. *J. Am. Chem. Soc.* **1968**, *90*, 1187. (b) Taube, H. *Pure Appl. Chem.* **1979**, *51*, 901. (c) Slep, L. D.; Pollak, S.; Olabe, J. A. *Inorg. Chem.* **1999**, *38*, 4369.

(6)   (a) Chen, Y.; Shepherd, R. E. *Inorg. Chem.* **1998**, *37*, 1249. (b) Krumm, M.; Zangrando, E.; Randaccio, L.; Menzer, S.; Lippert, B. *Inorg. Chem.* **1993**, *32*, 700.

(7)   See, e.g.: (a) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *Angew. Chem. Int. Edit.* **1995**, *34*, 1895. (b) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Am. Chem. Soc.* **1995**, *117*, 4562. (c) Lu, J.; Paliwala, T.; Lim, S. C.; Yu, C. ; Niu, T. ; Jacobsen, A. B. *Inorg. Chem.* **1997**, *36*, 923. (d) Tong, M.-L.; Chen, X.-M.; Yu, X.-L.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1998**, 5. (e) Kondo, M.; Okubo, T.; Asami, A.; Noro, S.-i.; Yoshitoni, T.; Kitagawa, S.; Ishii, T.; Matsuzaka, H.; Seki, K. *Angew. Chem. Int. Edit.* **1999**, *38*, 140. (f) Carlucci, L.; Ciani, G.; Porta, F.; Proserpio, D. M.; Santagostini, L. *Angew. Chem. Int. Edit.* **2002**, *41*, 1907. (g) Kumagai, H.; Kawata, S.; Kitagawa, S. *Inorg. Chim. Acta* **2002**, *337*, 387. (h)

Manson, J. L.; Arif, A. M.; Miller, J. S. *Chem. Commun.* **1999**, 1479. (i) Kraft, S.; Hanuschek, E.; Beckhaus, R.; Haase, D.; Saak, W. *Chem. Eur. J.* **2005**, *11*, 969.

(8)   For coordination polymers involving substituted pyrazine ligand see, e.g.: Näther, C.; Wriedt, M.; Jess, I. *Inorg. Chem.* **2003**, *42*, 2391 and refs. cited.

(9)   (a) Iengo, E.; Mestroni, G.; Geremia, S.; Calligaris, M.; Alessio, E. *J. Chem. Soc., Dalton Trans.* **1999**, 3361. (b) Komeda, S.; Kalayda, G. V.; Lutz, M.; Spek, A. L.; Yamanaka, Y.; Sato, T.; Chikuma, M.; Reedijk, J. *J. Med. Chem.* **2003**, *46*, 1210.

(10)   (a) Slone, R. V.; Hupp, J. T.; Stern, C. L.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **1996**, *35*, 4096. (b) Rajendran, T.; Manimaran, B.; Lee, F.-Y.; Lee, G.-H.; Peng, S.-M.; Wang, C. M.; Lu, K.-L. *Inorg. Chem.* **2000**, *39*, 2016.

(11)   Lau, V. C.; Berben, L. A.; Long, J. R. *J. Am. Chem. Soc.* **2002**, 124, 9042.

(12)   (a) Schweiger, M.; Seidel, S. R.; Arif, A. M.; Stang, P. J. *Angew. Chem. Int. Edit.* **2001**, *40*, 3467. (b) Yu, X.-Y.; Maekawa, M.; Kondo, M.; Kitagawa, S.; Jin, G.-X. *Chem. Lett.* **2001**, 168.

(13)   Raudaschl, G.; Lippert, B.; Hoeschele, J. D.; Howard-Lock, H. E.; Lock, C. J. L.; Pilon, P. *Inorg. Chim. Acta* **1985**, *106*, 141.

(14)   Dhara, S. C. *Indian J. Chem.* **1970**, *8*, 193.

(15)   Kauffman, G. B.; Cowan, D. O. *Inorg. Synth.* **1963**, *7*, 239.

(16)   Tribolet, R.; Sigel, H. *Eur. J. Biochem.* **1987**, *163*, 353.

(17)   Martin, R. B. *Science* **1963**, *139*, 1198.

(18)   *KappaCCD package*; Nonius: Delft, The Netherlands, 1997.

(19)   Otwinowsky, Z.; Minor, W. DENZO and SCALEPACK. *Methods Enzymol.* **1997**, *276*, 307.

(20)   Sheldrick, G. M. *SADABS*, Bruker AXS Inc.; Madison, WI, 2000.

(21)   Sheldrick G. M. *SHELXTL-PLUS (VMS)*, Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1990; *SHELXL-93, Program for crystal structure refinement*; University of Göttingen: Göttingen, 1993, *SHELXL-97, Program for the refinement of crystal structures*; University of Göttingen: Göttingen, 1997.

(22)   Maresca, L.; Natile, G.; Fanizzi, F. P. *J. Am. Chem. Soc.* **1989**, *111*, 1492.

(23)   Desiraju, G. R.; Steiner, T. *The Weak Hydrogen Bond*, Oxford University Press: Oxford, 1999.

(24)   Sigel, R. K. O.; Freisinger, E.; Metzger, S.; Lippert, B. *J. Am. Chem. Soc.* **1998**, *120*, 12000.

(25)   (a) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502. (b) Olenyuk, B.; Fechtenkötter, A.; Stang, P. J. *J. Chem. Soc., Dalton Trans*. **1998**, 1707.

(26)   Stang, P. J.; Cao, D. H. *J. Am. Chem. Soc.* **1994**, *116*, 4981.

(27)   (a) Rauter, H.; Hillgeris, E. C.; Erxleben, A.; Lippert, B. *J. Am. Chem. Soc.* **1994**, *116*, 616. (b) Rauter, H.; Hillgeris, E. C.; Lippert, B. *J. Chem. Soc., Chem. Commun.* **1992**, 1385.

(28)   (a) Schnebeck, R. D.; Freisinger, E.; Glahé, F.; Lippert, B *J. Am. Chem. Soc.* **2000**, *122*, 1381 and refs. cited. (b) Beck, B.; Schneider, A.; Freisinger, E.; Hothenrich, D.; Erxleben, A.; Albinati, A.; Zangrando, E.; Randaccio, L.; Lippert, B. *Dalton Trans*. **2003**, 2533.

(29)   Bing, X.; Dong, C.; Wenxia, T.; Kaibiei, Y.; Zhongyuang, Z. *Acta Cryst.* **1991**, *C47*, 1805.

(30)   Literature value 0.6; c.f. Toma, H. E.; Stadler, E. *Inorg. Chem.* **1985**, *24*, 3085.

(31)   Priqueler, J. R. L.; Rochon, F. D. *Inorg. Chim. Acta* **2004**, *357*, 2167.

(32)   Albinati, A.; Isaia, F.; Kaufmann, W.; Sorato, C.; Venanzi, L. M. *Inorg. Chem.* **1989**, *28*, 1112.

(33)   (a) Schnebeck, R. D.; Freisinger, E.; Lippert, B. *J. Chem. Soc., Chem. Commun.* **1999**, 675. (b) Schnebeck, R. D.; Freisinger, E.; Lippert, B. *Angew. Chem. Int. Edit.* **1999**, *38*, 168. (c) Schnebeck, R. D.; Freisinger, E.; Glahé, F.; Lippert, B. *J. Am. Chem. Soc.* **2000**, *122*, 1381.

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

	1	3	4b	5	7
chemical formula	$C_8H_{14}N_8O_6Pt$	$C_8H_{14}N_8O_6Pt$	$C_4H_{16}Cl_4N_6O_8Pt_2$	$C_{16}H_{47.33}N_{24}O_{27.67}Pt_4$	$C_{28}H_{48}Cl_5N_{12}O_{22}AgPt_2$
fw, g mol^{-1}	513.36	513.36	808.21	1799.05	1580.08
space group	P2$_1$/n (No. 14)	P2$_1$/n (No. 14)	P-1 (No. 2)	C2/c (No. 15)	C2/c (No. 15)
a, Å	5.810(1)	7.860(2)	10.429(2)	22.287(4)	34.927(7)
b, Å	15.870(3)	11.126(2)	10.488(2)	18.922(4)	10.663(2)
c, 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
1 V, Å^3	1511.6(5)	761.7(3)	854.2(3)	13416(4)	4960.6(17)
2 Z	4	2	2	12	4
3 T, K	293(2)	293(2)	163(2)	100(2)	120(2)
4 λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073
5 D$_{calcd}$, g cm^{-3}	2.256	2.238	3.142	2.682	2.116
6 μ, mm^{-1}	9.329	9.256	17.032	12.592	6.374
7 final R indices [I > 2σ(I)]^a	R1 = 0.0396, wR2 = 0.0940	R1 = 0.0178, wR2 = 0.0372	R1 = 0.0208, wR2 = 0.0510	R1 = 0.0395, wR2 = 0.0467	R1 = 0.0304, wR2 = 0.0531
8 R indices (all data)^a	R1 = 0.0620, wR2 = 0.0975	R1 = 0.0395, wR2 = 0.0397	R1 = 0.0238, wR2 = 0.0522	R1 = 0.1623, wR2 = 0.0593	R1 = 0.0534, wR2 = 0.0593

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

Table 2. ^{1}H NMR Data of Pyrazine Complexes in D$_2$O, pD 3 - 5

Comp	δH2,H2'^{a} $J(^{195}\text{Pt-}^1\text{H})^{b,c}$	δH3,H3'^{a} $J(^{195}\text{Pt-}^1\text{H})^{b,d}$	δCH$_2$ $J(^{195}\text{Pt-}^1\text{H})^{b,c}$	δCH$_3$ $J(^{195}\text{Pt-}^1\text{H})^{b,c}$
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 multiplet
^{b} in Hz
^{c} ^3J coupling
^{d} ^4J coupling
^{e} ^{195}Pt satellites not observed

Figure Legends

Figure 1.   View of *cis*-[(NH$_3$)$_2$Pt(pz)$_2$](NO$_3$)$_2$ (**1**). Selected structural details (distances in [Å], angles in [°]): 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 *trans*-[(NH$_3$)$_2$Pt(pz)$_2$](NO$_3$)$_2$ (**3**) Selected structural details (distances in [Å], angles in [°]): Pt-N11, 2.011(3); Pt-N1, 2.041(3); N11-Pt-N1, 88.98(12).

Figure 3.   Hydrogen bonding between pz ligands of **1**. Intermolecular distances between N and C sites are 3.283(9) Å (rings a and a*) and 3.264(8) Å (rings b and b*).

Figure 4.   View of *cis*-[{(NH$_3$)$_2$PtCl}$_2$(pz)](ClO$_4$)$_2$ (**4b**). Selected structural details (distances in [Å], angles in [°], see also 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).

Figure 5.   Side and top view of pairs of cations of **4b**.

Figure 6.   View of cation of open pyrazine box *cis*-[{(NH$_3$)$_2$Pt(pz)}$_4$]$^{8+}$ (**5**). Only one of two crystallographically independent cations (I) is depicted.

Figure 7.   Detail of interaction of cation (I) of **5** with nitrate anion N(30), which is partially inserted in the open pyrazine box. Oxygen atom O33 is pointing toward the center of the box, while O31 makes a contact with a Pt from a neighboring cation.

Figure 8.   View centrosymmetric cation [{(tmeda)Pt(pz)$_2$}$_2$Ag]$^{5+}$ (**7**).

Figure 9.   Interactions of Z-shaped cations of **7** to produce an extended structure of open pyrazine boxes. The views are perpendicular to the array of the boxes.

Figure 10: Partial insertion of perchlorate anion $Cl(1)O_4^-$ in $Pt_2Ag_{2/2}$ box. The oxygen atom sticking furthest out of the box (O31) forms a long contact to an Ag^+ ion in the tape above.

Figure 11. 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.
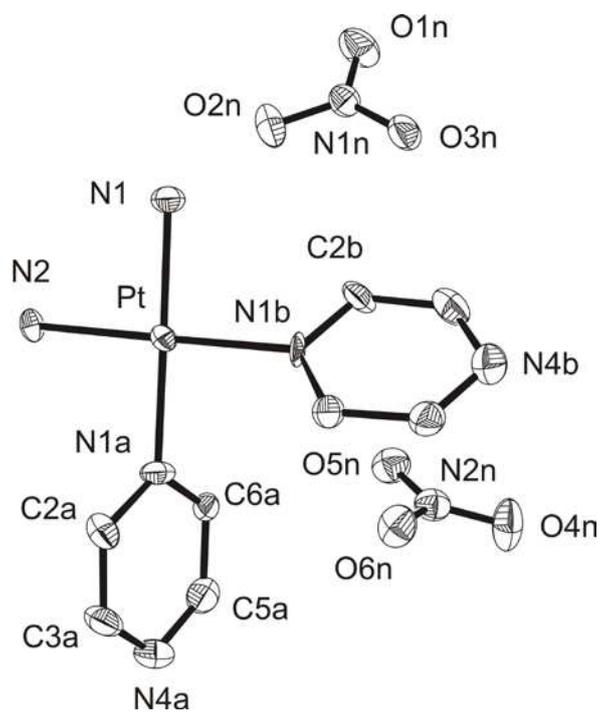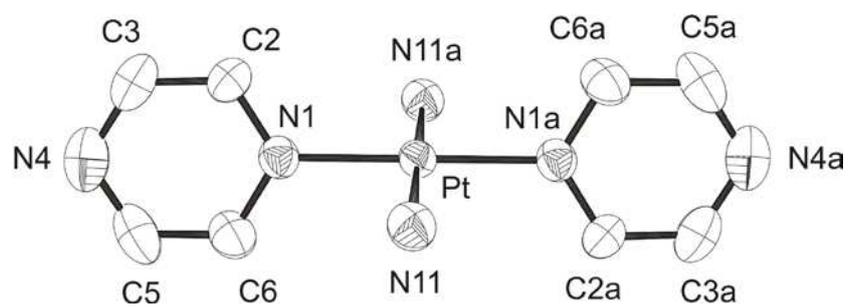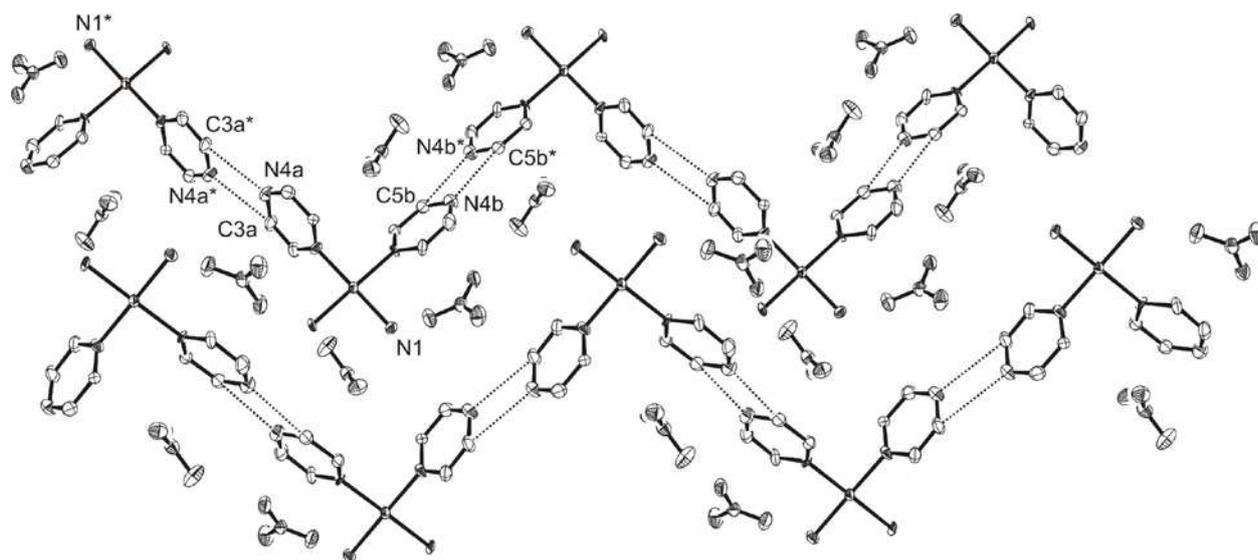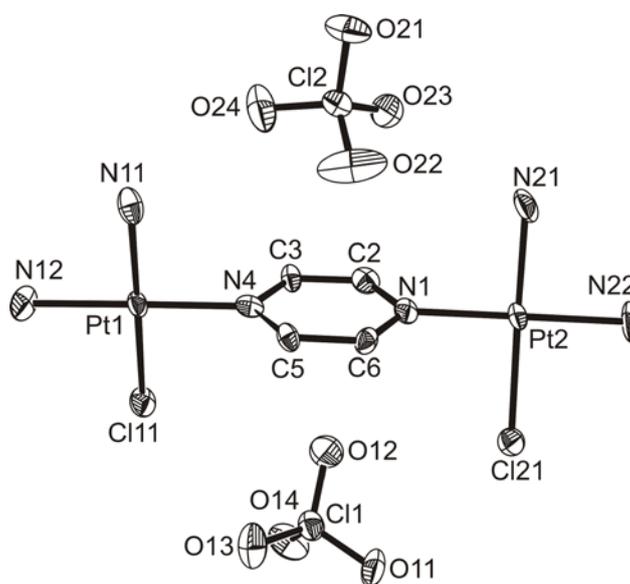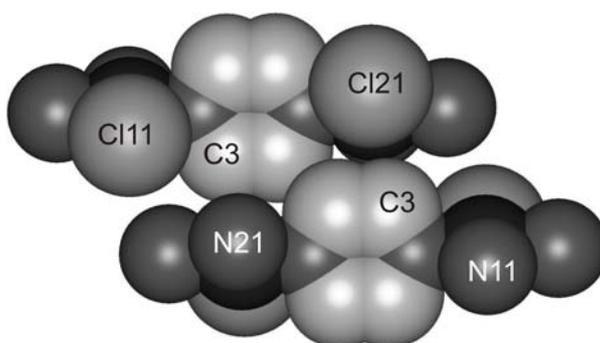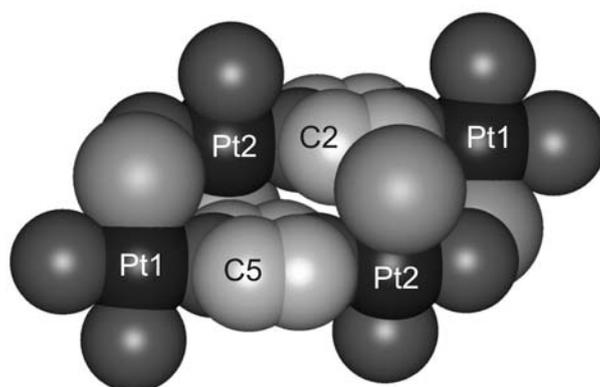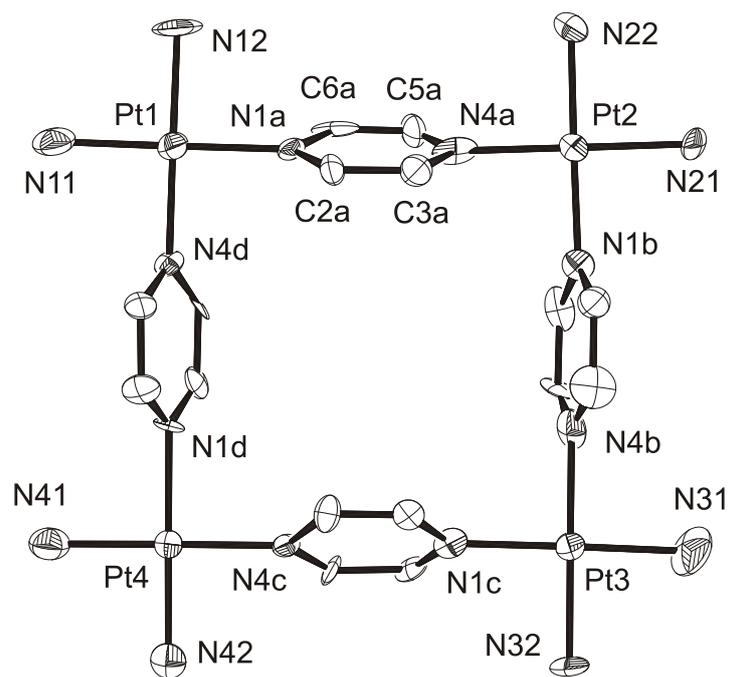
Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6
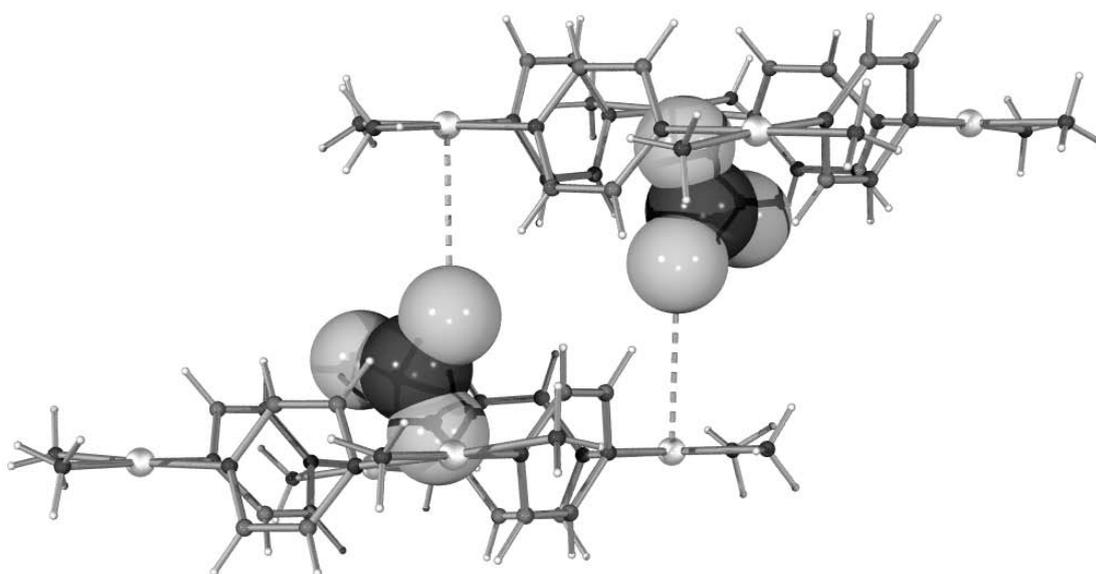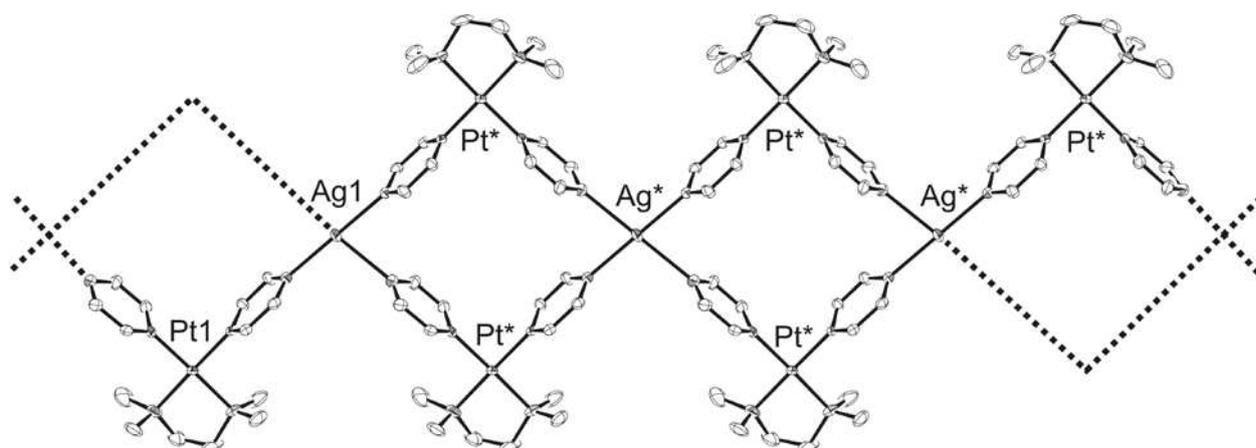
Figure 7
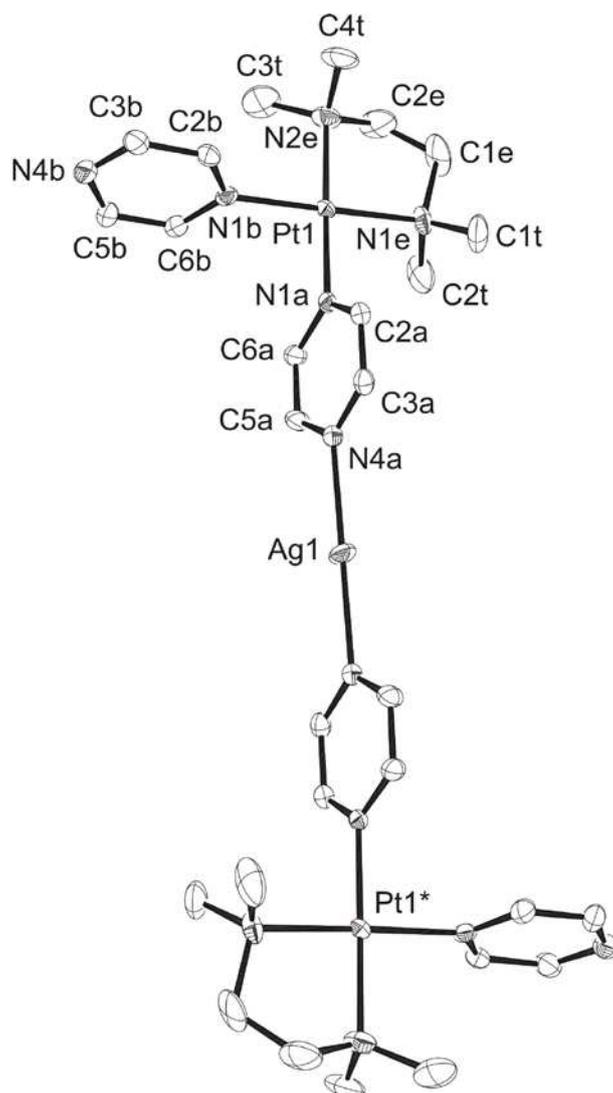
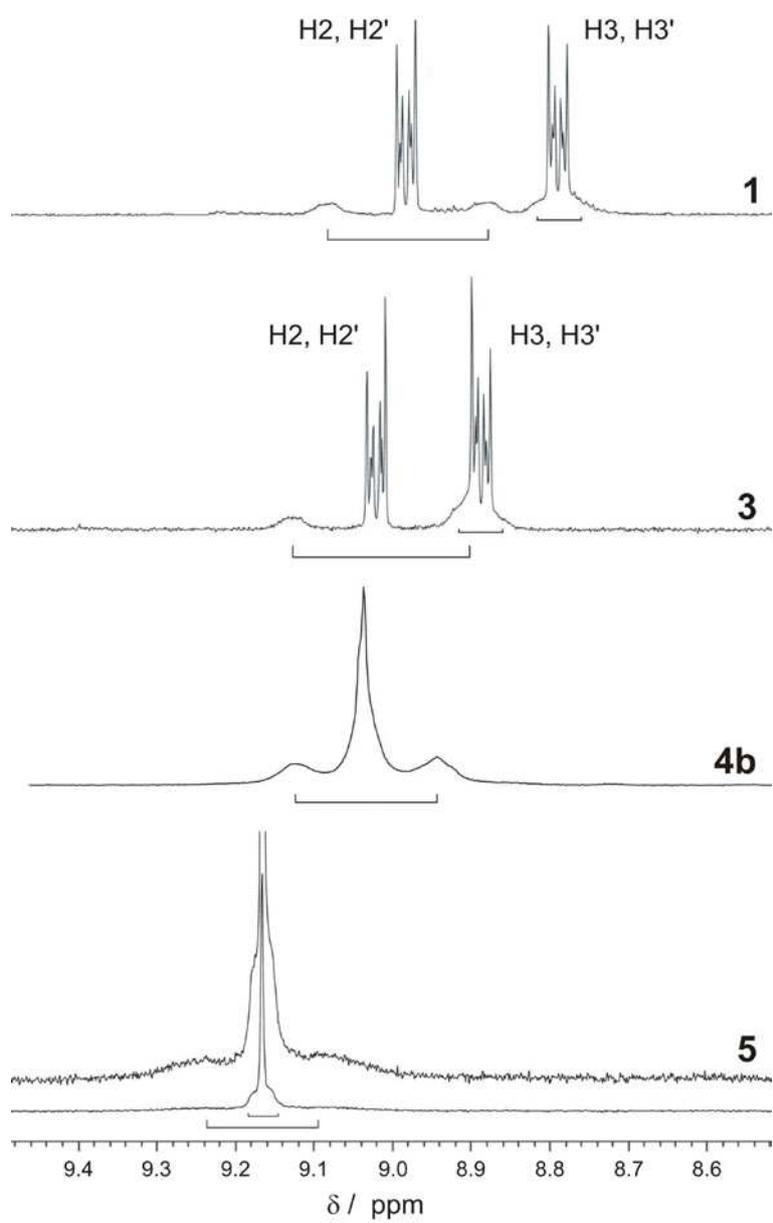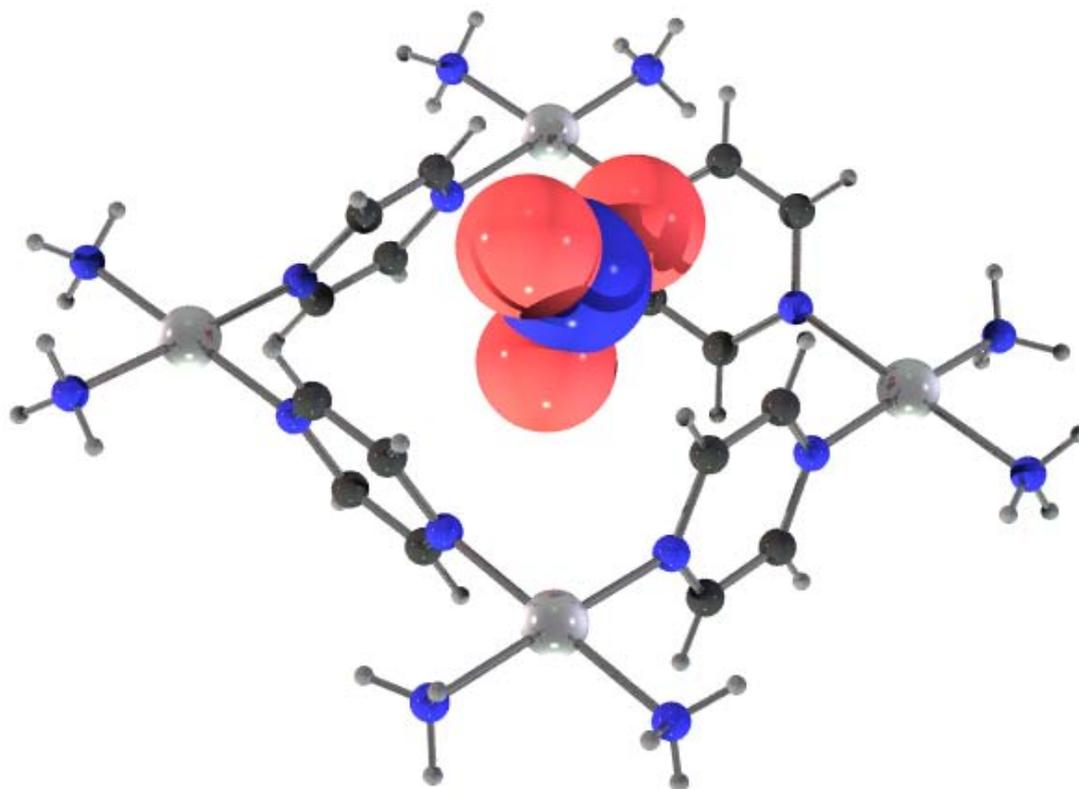**Figure 8**
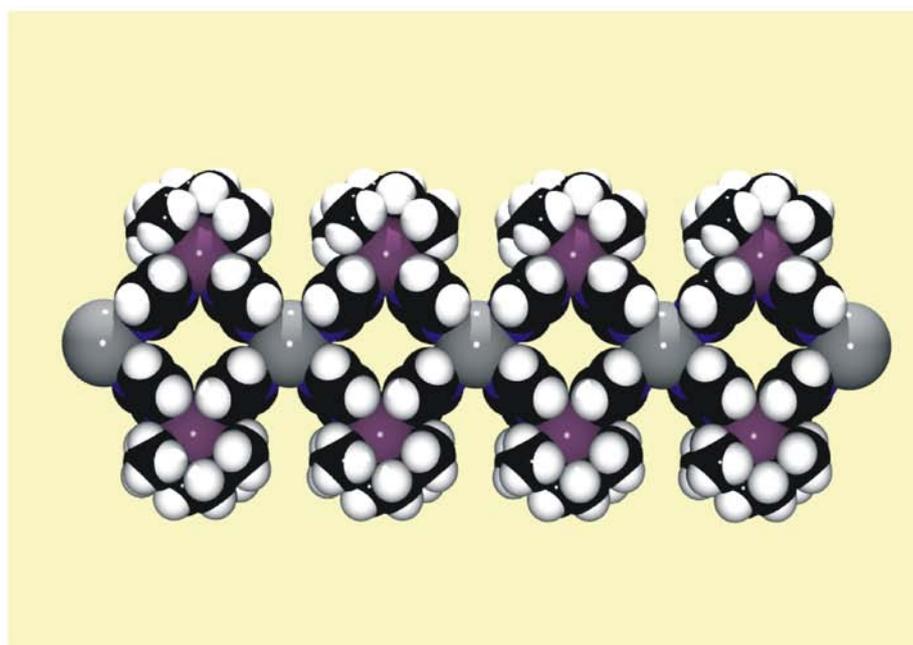
Figure 9

Figure 10

Figure 11

Table of Contents

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[*]

The cationic, open molecular box derived from Cisplatin and pyrazine, *cis*-[{(NH$_3$)Pt(pz)}$_4$](NO$_3$)$_8$·3H$_2$O partially inserts a nitrate anion.