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Synthesis and molecular structure of N-methylpiperazinium(+1) and N,N'-dimethylpiperazinium(+2) platinum(II) and platinum(IV) complexes Part II

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Abstract

Square-planar Pt(11) and octahedral Pt(1V) ionic complexes $[H_2Me_2ppz]^{2+}$ [PtCl₄]²⁻ (1), $[PtCl_3(H_2Me_2ppz)]_2[H_2Me_3ppz]^{2+}$ [PtCl₄]²⁻ ·2H₂O (2) and $[H_2Me_2ppz]^{2+}$ [PtCl₆]²⁻ (3) have been synthesized and their molecular structure and geometry investigated through X-ray diffraction. The *N*-methylpiperazinium(+1) ligand bound to Pt(II) in complex 2 and the dipositive *N*,*N'*-dimethylpiperazinium(+2) cation in complexes 1, 2 and 3 are always present in the energetically favoured chair conformation. Moreover the crystals of complex 2 show an unusual situation containing at the same time [PtCl₃(H₂Meppz)]₂ amphilonic molecules and [H₂Me₂ppz]²⁺ [PtCl₄]²⁻ ions, \oplus 1998 Elsevier Science S.A. All rights reserved.

Keywonds: Crystal structures; Platinum complexes; Piperazine complexes

1. Introduction

In the first part of this research [1] we have presented three complexes formed by Pt(II) with the positively charged *N*methylpiperazinium(+1) cationic ligand, $[H_2Meppz]^+$, or with the neutral *N*,*N'*-dimethylpiperazine ligand, Me₂ppz. The former ligand binds to Pt(II) as monodentate at the N-H nitrogen site with piperazine ring in the usual chair conformation, whereas the latter ligand binds to Pt(II) as chelate through the methylated nitrogen atoms of neutral piperazine ring in the rare boat conformation. Here we present some chemical results, including X-ray molecular structures, on ionic complexes formed by *N*,*N'*-dimethylpiperazinium(+2) cations and by $[PtCl_4]^{2-}$ or $[PtCl_6]^{2-}$ anions. In particular, compound 2 is interesting as it is formed by $[PtCl_3(H_2Meppz)]$ amphilonic molecules and $[H_2Me_2-$ $\begin{array}{l} ppz]^{2+} \left[PtCl_4 \right]^{2-} \text{ ions; thus it is at the same time a molecular} \\ \text{and an ionic crystal. The compounds can be formulated} \\ \text{as } \left[H_2 Me_2 ppz \right]^{2+} \left[PtCl_4 \right]^{2-} (1), \left[PtCl_3 (H_2 Meppz) \right]_{2^-} \\ \left[H_2 Me_2 ppz \right]^{2+} \left[PtCl_4 \right]^{2-} \cdot 2H_2 O(2) \text{ and } \left[H_2 Me_2 ppz \right]^{2+} \\ \left[PtCl_6 \right]^{2-} (3). \end{array}$

2. Experimental

2.1. Materials and instruments

Commercial reagent grade chemicals N,N'-dimethylpiperazine, Me₂ppz, (98%, Aldrich) and potassium tetrachloroplatinate(II) (K₂PtCl₄) and hexachloroplatinate(IV) (K₂PtCl₆) (Fluka) were used without further purifications.

Far-IR spectra (400–50 cm⁻¹) were recorded for Nujol mulls on a Nicolet 5Sxc FT-IR (20 far IR) spectrometer. X-ray data were collected on a Philips PW 1100 diffractometer equipped with graphite-monochromated Mo K α radiation.

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2.2. Synthesis of the complexes

2.2.1. [H2Me2 ppz]2+[PtCl4]2-(1)

This compound was obtained by (a) direct reaction of K_2PtCl_4 with diprotonated N,N'-dimethylpiperazine, H_2Me_2ppz , or (b) as by product in the formation of *cis*-[PtCl_2(Me_2ppz)] chelate complex starting from K_2PtCl_6 and an excess diamine which also causes the reduction to Pt(II) [1].

(a) Me₂ppz (0.050 cm³, 0.36 mmol) dissolved in water (15 cm³) and reacted with HCl 1 N (0.72 cm³, 0.72 mmol) was added to 25 cm³ of an aqueous solution of K₂PtCl₄ (0.149 g, 0.36 mmol). Red crystals which separated on slow concentration of the solution were collected, washed with EtOH, Et₂O, and dried under vacuum. Yield 0.111 g, 68%. *Anal.* Found: C, 15.7; H, 3.4; N, 6.0, Cl, 31.1. Calc. for C₆H₁₆N₂Cl₄Pt (1): C, 15.9; H, 3.6, N, 6.2; Cl, 31.3%.

(b) Me₂ppz (0.050 cm³, 0.36 mmol) dissolved in water (15 cm^3) and reacted with HCl 1 N (0.72 cm³, 0.72 mmol) was added to 25 cm³ of an aqueous solution of K₂PtCl₆ (0.175 g, 0.36 mmol) at 55°C. A yellow-orange compound precipitated, corresponding to $[H_2Me_2ppz]^{2+}$ [PtCl₆]²⁻ and subsequently identified as compound 3. After 24 h, the addition of a second equivalent of free base Me₂ppz (0.050 cm^3 , 0.36 mmol) to the solution dissolved the above-mentioned precipitate turning the colour of the solution to yellow. The resulting mixture was heated while stirring at 55°C for 4 h and then left for 3 days at room temperature. The yellow crystals which separated from the solution were collected and subsequently identified as the cis-[PtCl₂(Me₂ppz)] chelate complex, already characterized by us through X-ray analysis [1]. Red crystals, which were obtained by a further slow concentration of the solution, were collected, washed with EtOH, Et₂O, and dried under vacuum. Yield 0.037 g, 23%. Anal. Found: C, 15.9; H, 3.6; N, 6.1; Cl, 31.3. Cale. for $C_{0}H_{10}N_{3}Cl_{4}Pt(1)$; C, 15.9; H, 3.6, N, 6.2; Cl, 31,3%,

2.2.2. $(PtCl_{4}(H_{2}Meppz))_{2}(H_{2}Me_{2}ppz)^{2+}(PtCl_{4})^{2-1}2H_{2}O$ (2)

Red-brown crystals subsequently separated from the mother solution of 1. They were filtered, washed with EtOH, Et₂O, and dried under vacuum. Yield 0.027 g, 5%. Anal. Found: C, 14.8; H, 3.6; N, 6.5; Cl, 27.3. Calc. for $C_{10}H_{46}N_6O_2Cl_{10}Pt_3$ (2): C, 14.9; H, 3.6, N, 6.5; Cl, 27.4%. The elemental analysis and in particular the X-ray structure determination of this compound have shown that the piper-azinium ring is unexpectedly coordinated to Pt(II) through a nitrogen atom that has lost its methyl group (see discussion on compound 2).

2.2.3. [H2Me2ppz]²⁺[PtCl6]²⁻(3)

Me₂ppz (0.025 cm³, 0.18 mmol) dissolved in water (10 cm³) and reacted with HCl I N (0.36 cm³, 0.36 mmol) was added to 20 cm³ of an aqueous solution containing K₂PtCl₆ (0.0875 g, 0.18 mmol) at 55°C. The yellow solution was concentrated to about 10 cm³ and left at room temperature. After 4 days yellow-orange crystals were obtained. They were filtered, washed with water, EtOH, Et₂O, and dried under vacuum. Yield 0.160 g, 85%. *Anal*. Found: C, 13.8; H, 3.1; N, 5.3; Cl, 40.5. Calc. for $C_6H_{16}N_2Cl_6Pt$: C, 13.7; H, 3.1; N, 5.4; Cl, 40.6%.

2.3. X-ray crystallographic procedures

Crystal data, data collection and refinement parameters for compounds 1-3 are summarized in Table 1. The same procedure described in Part I [1] has also been used for the Xray data collection and refinement of the present three compounds except that (i) the absorption corrections were applied using the X ABS2 program [2] after several leastsquares cycles with isotropic thermal parameters, and (ii) the intensities of compound 2 were corrected for a slight increase with time as pointed out by the three standard reflections. Hydrogen atoms were introduced in idealized positions for the calculation of structure factors prior to least-squares cycles with C-H = 0.97 Å for methylene hydrogen atoms. N-H = 0.91 Å for amine hydrogen while the C-H methyl hydrogen distance was restricted to 0.96 Å with an e.s.d. of 0.02 Å. All crystallographic calculations were performed with the SHELXL-93 [3] and PARST [4] programs and molecular graphics with ORTEPII [5] or ORTEX [6] programs. Bond lengths and angles for the three crystal structures, along with their e.s.d.s, are listed in Tables 2-4.

3. Results and discussion

3.1. Molecular structure of complexes 1-3

Here, the common structural features of compounds 1-3 are discussed, while their specific characteristics will be reported later. The Pt-Cl distances are substantially constant differing at the most by ± 0.016 Å from the mean value of 2.312(5) Å, which is comparable with values found in similar complexes with or without a small structural *trans* influence.

A particular discussion is devoted to the $[PtCl_4]^{2-}$ anion present in complexes 1 and 2. The mean Pt–Cl distances, 2.303(3) Å in 1 and 2.302(7) Å in 2, practically coincide or are comparable with the values observed in similar complexes, namely 2.292(2)–2.298(2) Å in $[C_{10}H_{24}N_4S_2]$ [PtCl₄] [7], 2.305(2)–2.306(1) Å in $[PtCl_2(C_3H_{10}N_2)]$ [PtCl₄] [8], 2.294(5) Å (mean) in (Hthiamin) [PtCl₄] [9] and 2.308(2)–2.318(2) Å in $(C_{10}H_{24}N_4P_3)_2$ [PtCl₄] [10]. The [PtCl₄]²⁻ anion found in both 1 and 2 has the Pt atom situated on a centre of symmetry and an extensive hydrogen bonding network as frequently shown by such an anion. Another characteristic of the tetrachloroplatinate(II) anion is that it is perfectly planar even if it is not placed on a centre of symmetry.

The unique Pt(II)--N distance of 2.09(1) Å found in 2 is nearly in agreement with that of 2.08(2) Å observed in

Table I

 $Crystallographic data of [H_2Me_2ppz]^{2+} [PtCl_4]^{2-} (1), [PtCl_4(H_2Meppz)]_2 [H_2Me_2ppz]^{2+} [PtCl_4]^{2-} 2H_2O (2) and [H_2Me_2ppz]^{2+} [PtCl_6]^{2-} (3)$

Complex	1	2	3	
Formula	[C ₆ H ₁₆ N ₂] ²⁺ [PtCl ₄] ²⁺	$[PtCl_3(C_5H_{13}N_2)]_2[C_6H_{16}N_2]^{2+}-$ $[PtCl_4]^{2-}2H_3O$	$[C_6H_{16}N_2]^2$ $[PtCl_6]^2$	
Molecular weight	453.10	1294	524.00	
Crystal size (mm)	0.10×0.15×0.20	0.20×0.30×0.30	0.10×0.10×0.10	
Crystal colour	red	red-brown	yellow-orange	
Crystal system	monoclinic	monoclinic	orthorhombic	
Space group	C2/c (No. 15)	$P2_1/a$ (No. 14)	Pnnm (No. 58)	
a (Å)	13.737(3)	25.774(9)	9.606(2)	
b (Å)	7.901(2)	8.427(3)	9.113(2)	
c (Å)	12.898(3)	8.345(3)	8.717(2)	
β(°)	115.60(6)	98.77(10)		
V (Å3)	1262.5(8)	1791.3(1.1)	763.1(3)	
Ζ	4	2	2	
<i>D_c</i> (g cm ⁻³)	2.384	2.400	2.281	
λ (Å), μ (Μο Κα) (mm 1)	0.7107; 11.92	0.7107; 12.46	0.7107; 10.22	
Relative transmission factors	0.82-1.00	0.87-1.00	0.91~1.00	
Temperature (K)	293(2)	293(2)	293(2)	
F (000)	848	1208	492	
2θ range (°)	6.12-49.98	4.94-50.02	6.16-55.98	
No. measured reflections	2233	3814	1100	
No. unique reflections (n)	1116	3114	984	
Indices of observed reflections	h(-16/14), k(0/9), l(0/15)	h(-30/30), k(0/10), l(0/9)	h(0/12), k(0/12), l(0/11)	
Reflections with $l > 2\sigma(l)$	936	2470	764	
No. parameters refined (p)	61	187	46	
$R1^{a}, wR2^{b}([1>2\sigma(1)])$	0.0387, 0.1032	0.0653, 0.1639	0.0217, 0.0552	
k1, wR2	0.0451, 0.1087	0.0926; 0.1747	0.0368, 0.0590	
Goodness-of-fit *	0.957	0.979	1.013	
g in weighting scheme ⁴	0.1189	0.1533	0.0447	
Mean shift (e.s.d.)	0.001	0.006	0.001	
Highest peak, hole (e Å ⁻¹)	1.70, -1.85	2.00, -2.00	1.03, =0.89	

 ${}^{*}R = \Sigma(|F_{i}| - |F_{i}|)/\Sigma|F_{i}|.$

⁴ wR2 = { $\sum w [(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2]$ }^{1/2}.

 $GOF = S = \left(\sum w \left[\left(F_n^2 - F_n^2 \right)^2 \right] / (n - p) \right)^{1/2}.$

 $d w = 1/(\sigma^2(F_0^3)^2 + (gP)^2)$, $P = [\max_{i}(F_0^{-2}) \circ r(0) + 2(F_0^{-2})]/3$, n = number of unique reflections; p = number of parameters refined.

Table 2

Bond lengths (Å) and angles (") for $[H_2Me_2ppz]^{2+}[PtCl_4]^{2+}(1)$, with e.s.d.s in parentheses

Pt=C1(1)	2.305(3)	Cl(1) = Pl = Cl(2)	90.43(10)
Pt=C1(2)	2.301(2)	$Cl(1)=Pt=Cl(2)^{1}$	89.57(10)
N(1)-C(1)	1.500(8)	C(1)=N(1)=C(2)	111.0(5)
N(1) - C(2)	1.477(8)	C(1)-N(1)-C(3)	111.2(6)
N(1)-C(3)	1.495(11)	C(2)-N(1)-C(3)	111.7(7)
C(1)C(2) ¹¹	1.502(9)	$N(1)-C(1)-C(2)^{11}$	110.9(5)
		$N(1)-C(2)-C(1)^{11}$	111.5(5)

Torsion angles

 $N(1)-C(1)-C(2)^{H}-N(1)^{H}_{E2} = 55.6(7)$

Angles between LQS planes C(1)-N(1)-C(2)^C(1)-C(2)-C(1)¹¹-C(2)¹¹ \approx 129.8(4)

Angles between LQS lines C(1)-C(2)^{#∧}N(1)-C(3) = 179.6(7)

Symmetry transformations used to generate equivalent atoms: $^{1} = (-x, -y, -z)$; $^{0} = (1/2 - x, -1/2 - y, -z)$.

[PtCl₃(H₂Meppz)] and differs by only 0.03 Å from the mean value of 2.06(1) Å found for all platinum piperazine complexes already described [1]. Furthermore, it is comparable

with the values observed for other platinum(11) amine complexes: 2.055(1) Å (mean) in [{cis-Pt(NH₃)₂}₄($\mu_{4^{-}}$ CO₃)₂]⁴⁺ [11], 2.055(4) Å in [Pt(NH₃)₄]²⁺ [12], 2.037(9) Å in [Pt(en)₂]²⁺ (en=ethylenediamine) [13], 2.055(6) Å in [Pt(pn)₂]²⁺ (pn=propanediamine) [14] and 2.084(9) Å in [cis-[PtCl₂(NH₃)(etanidazole)]₄ [15].

The conformations of the piperazine ring, in piperazine itself, in N-methylpiperazinium(+1) or in N-methylpiperazine, have been extensively discussed in Section 3.1 of Ref. [1]. Now we discuss the theoretical conformations of N.N'dimethylpiperazinium(+2) cation (but also N,N'-dimethylpiperazine) which can, in principle, exhibit three possible chair conformations [16] in which N-H (or N-lone pair) and N-CH₃ bonds may respectively be: (a) equatorial and axial for both the nitrogen atoms with a 2/m point group; (b) axial and equatorial for one nitrogen atom and vice versa for the other one with only an m point group; (c) axial and equatorial for both the nitrogen atoms with again a 2/m point group. The N,N'-dimethylpiperazinium(+2) cation was found to be always in the (c) conformation. This is a consequence of the higher steric hindrance of methyl group with respect to the hydrogen atom. Moreover, axial hydrogen

Table 3

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			• N.C	+ (D. () 12 -	<u>100 (1)</u>	ith a c d o in nononthoooc
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ROMA MADDINS CA			11110170101111111102PPPP	1		
						=

In [PtCl ₁ (H ₂ Meppz)] ₂			
Pt(1)-Cl(1)	2.320(5)	N(2)-C(2)	1.54(3)
Pt(1)-Cl(2)	2.315(5)	N(2)-C(3)	1.50(2)
Pt(1)-Cl(3)	2.313(4)	N(2)-C(5)	1.50(2)
Pt(1)-N(1)	2.09(1)	C(1)-C(2)	1.51(3)
N(1)-C(1)	1.49(2)	C(3)-C(4)	1.53(3)
N(1)-C(4)	1.46(3)		
C(1) - P(1) - N(1)	175.6(4)	C(1)-N(1)-C(4)	110.3(1.4)
$C_{1}(2) = P_{1}(1) = N(1)$	93.2(4)	N(1)-C(1)-C(2)	112.3(1.4)
C(3) - Pt(1) - N(1)	86.5(4)	N(1)-C(4)-C(3)	111.0(1.6)
Ci(1) = Pt(1) = Ci(2)	89.8(2)	C(1)-C(2)-N(2)	109.9(1.5)
Cl(1) = Pt(1) = Cl(3)	90.8(2)	C(2)-N(2)-C(3)	110.2(1.4)
C(2) = P(1) = C(3)	176.0(2)	C(2)-N(2)-C(5)	110.8(1.6)
Pt(1) - N(1) - C(1)	112.2(1.0)	C(3)-N(2)-C(5)	112.7(1.5)
Pt(1)=N(1)=C(4)	116.8(1.2)	N(2)-C(3)-C(4)	111.2(1.5)
Torsion angles inside the coord	dinated piperazine ring		
N(1) = C(1) = C(2) = N(2) = -56.0(2.1)		N(2)-C(3)-C(4)-N(1) = 57.7(2.1)	

N(1)=C(1)=C(2)=N(2) = -56.0(2.1)

LOS planes

Deviations ($A \times 10^3$) in square brackets from the weighted least-square plane through the started atoms Pr(1) * [-21]; Cl(1) * [-19]; Cl(2) * [58]; Cl(3) * [59]; N(1) * [-147]; N(2) [336]; C(5) [179]; C(1) [1166]; C(2) [1037]; C(3) [-970]; C(3) [-970C(4) [-773]. P(1) * [-33]; C(1) * [28]; C(2) * [43]; C(3) * [50]; N(1) * [-213]; CM14 * [113]; CM23 * [-88]; N(2) * [196]; C(5) * [2]; C(1)[1085]; C(2) [917]; C(3) [-1093]; C(4) [-858].(CM14 and CM23 are the midpoints between C(1)-C(4) and C(2)-C(3) respectively)

Angles between LQS planes

 $Pt(1)-Cl(1)-Cl(2)-Cl(3)-N(1)^N(1)-CM14-CM23-N(2)-C(5) = 35.7(1.7)$ $P_1(1)=C_1(1)=C_1(2)=C_1(3)=N(1)^C(1)=C(2)=C(3)=C(4)=54.1(6)$

Analas hanvaan I AS lines

$\begin{array}{l} \text{C(1)=C(2)}^{N}(2)=C(5) \equiv 1.2(1.4)\\ \text{C(1)=C(2)}^{P}(1)=N(1) \equiv 10.0(1.1)\\ \text{C(3)=C(4)}^{N}(2)=C(5) \equiv 178.2(1.3) \end{array}$		C(3)~C(4) ^Pt(1)-N(1) = 1 Pt(1)=N(1) ^N(2)-C(5) = 9	$C(3) = C(4)^{Pt}(1) = N(1) = 170.9(1.2)$ $Pt(1) = N(1)^{N}(2) = C(5) = 9.8(1.0)$		
In [H3Me3ppz] ² * [PtCl4] ²					
Pt(2)=Cl(4)	2.309(7)	N(3)=C(8) *	1,54(3)		
P1(2)=Cl(5)	2.296(6)	Cl(4)=Pt(2)=Cl(5)	88.8(2)		

* We report here only the N(3) = C(8) distance as the other distances and angles are disordered (see discussion in the text).

Table 4

Bond lengths (Å) and angles (°) for $[H_2Me_2ppz]^{2+}$ [PtCL]²⁺ (3) with e.s.d.s in parentheses

Pt-Cl(1)	2.323(1)	Cl(1)PtCl(2)	90.77(4)
H=Ĉ(2)	2.329(2)	Cl(1)-Pt-Cl(1)"	89.53(5)
N(1)=C(1)	1.495(5)	C(2)-N(1)-C(1)	111.9(3)
N(1)=C(2)	1.492(8)	$C(1)^{m}-N(1)-C(1)$	110.5(4)
C(1)=C(1)	1.510(9)	N(1)-C(1)-C(1) ¹	110.3(3)

Torsion angles in the hexacyclic ring $N(1)=C(1)=C(1)^{1}=N(1)^{1}=57.7(4)$

Angles between LQS lines $C(1)=C(1)^{N}(1)=C(2)=176.6(4)$

Symmetry transformations used to generate equivalent atoms: '=(-x, -x)1 = y, z; H = (x, y, -z); H = (x, y, 1-z).

allows the formation of intramolecular hydrogen bonds with a further stabilizing effect on the piperazine molecule.

Another interesting feature exhibited by compounds 1 and 2 is that, along the z direction, there are one or two hydrogen atoms with Pt...H distances: 1, 2.83 and 2.96 Å; 2, 3, 12, 3.24 and 3.02 Å.

Finally, in these complexes the piperazine ring always shows the highest possible protonation state as the acidity conditions used lead to the formation of piperazinium cations. In compound 2, the N-methylpiperazinium(+1) ion, even if positively charged, is capable of coordinating the platinum(II) atom, a situation already found in [1]. The donor properties of positively charged ligands have been discussed since 1969 [17-20].

3.2. Single crystal structure of $[H_2Me_2ppz]^2 + [PtCl_4]^2$ (1)

Bond lengths and angles of complex 1 are reported in Table 2. The crystal contains discrete $[H_2Me_3ppz]^{2+}$ diprotonated cations and $[PtCl_4]^{2-}$ anions as illustrated in Fig. 1. The Pt atom is situated on the centre of symmetry at (0, 0, 0)while the centre of the dipositive piperazinium cation coin-



Fig. 1. ORTEP diagram for [N,N'-dimethylpiperazinium(+2)] [tetrachloroplatinate(II)], $[H_2Me_2ppz]^{2+}$ [PtCl₄]²⁺ (1) with the atomic numbering scheme used. The hydrogen bonds are indicated by broken lines. The displacement ellipsoids are drawn at the 50% probability level and the selected H atoms are shown as spheres of arbitrary radii.

cides with the crystallographic centre of symmetry at (1/4, -1/4, 0) so that the C2/c monoclinic cell contains four $[PtCl_4]^{2-}$ anions and four $[C_6H_{10}N_2]^{2+}$ cations.

The two independent Pt-Cl distances are 2.305(3) and 2.301(2) Å, respectively (Table 2) and they are quite normal (see general discussion on $[PtCl_4]^{2-}$). The dipositive piperazinium cation possesses a six-membered ring in a chair conformation with the tetrahedral nitrogen atoms $\pm 0.628(8)$ Å out of the plane of the four C(1), C(2), C(1)¹ and C(2)¹ carbon atoms; ${}^{1}=(1/2-x, -1/2-y, -z)$. Moreover, as already pointed out in the general discussion, the N-H bond is axial and the N-CH₃ bond is equatorial for both the nitrogen atoms.

The three $C(sp^3) - N'(sp^3)$ bonds (average 1.491(9) Å) are slightly longer than the value of 1.479(6) Å found in $[C_4H_{12}N_2]^{2+}[HPO_4]^{2-} H_2O$ [21] but significantly longer than that for piperazine itself (1.467 Å) [22]. The $C(sp^3) - C(sp^3)$ bond of 1.502(9) Å is slightly longer than the value found in the above-mentioned compound (1.495(6) Å) [21] but shorter than that found in *N*,*N'*-dimethylpiperazine (1.521 Å) [23], in *cis*-DDP (1.535 Å) [24], in *trans*-DDP (1.517 Å) [25] or in *trans*-2,5-dimethylpiperazine (1.521 Å) [26]. All interior angles are approximately tetrahedral and average 111.3(6)°.

Crystal packing is dominated by an N⁺-H···C₁(1) hydrogen bond of 3.170(7) Å with an N⁺-H···Cl(1) angle of 162.1(6)°. This hydrogen bond connects N,N'-dimethylpiperazinium dipositive cations with [PtCl₄]²⁻ anions forming infinite chains of the type ···[PtCl₄]²⁻ ··· (CH₃-N⁺H-·C₄H₈-N⁺H-·CH₃)···[PtCl₄]²⁻ ··· running along the [1 - 1 0] direction. Also in this case there are short contacts between the Pt atom and the hydrogen atoms along the z direction of the platinum(II) d_{z²} orbital: Pt···H(1)¹=2.83(1) Å (¹= -x, -y, -z) and Pt···H(2)B^{II}=2.95(1) Å (^{II}= -1/2 +x, 1/2+y, z). All other intermolecular contacts are in the normal van der Waals range.

3.3. Single crystal structure of $[PtCl_3(H_2Meppz)]_2$ - $[H_2Me_2ppz]^{2+}[PtCl_4]^{2-} \cdot 2H_2O(2)$

Table 3 reports the bond lengths and angles of bis-[PtCl₃(monoprotonated N-methylpiperazinium(+1)] [diprotonated N,N'-dimethylpiperazinium(+2)]²⁺ tetrachloroplatinate(II) dihydrate (2). The X-ray diffraction study demonstrates that the cell with space group $P2_1/a$ contains four [PtCl₃(monoprotonated N-methylpiperazinium-(+1) neutral molecules in general position, two $[PtCl_4]^{2-}$ anions with the Pt atom situated on the centre of symmetry at (0, 0, 0), and two stand-alone centrosymmetric $CH_3-N^+H-(CH_2)_4N^+H-CH_3$ dipositive cations situated at (1/2, 0, 1/2), so that crystals are a mixture of the [PtCl₃(H₂) Meppz)] complex already reported in [1] and of the compound 1 of this work with a 2:1 molar ratio. Fig. 2 shows the mutual disposition of the two compounds. In spite of the difficulties encountered during data collection and structure refinement owing to instability of crystals under the X-ray beam and to disorder at the stand-alone piperazinium dipositive cation, several conclusions can be made about the geometry of such a molecule. The [PtCl₃(monoprotonated N-methylpiperazinium(+1) moiety is very similar to that already reported for $[PtCl_3(H_2Meppz)]$ alone [1]. The piperazine ring is in the chair conformation with the N(1)-C(1)-C(2)-N(2) and N(2)-C(3)-C(4)-N(1) ring torsion angles of -56.0 (2.1) and 57.7 (2.1)°, respectively. The N(2)-C(5) and Pt(1)-N(1) bonds are in the equatorial position as indicated by LQS lines in Table 3. Moreover, the whole molecule shows a very approximate mirror plane passing nearly through Pt(1), Cl(1), Cl(2), Cl(3), N(1) and nearly bisecting the piperazine ring; in fact the angle between the coordination plane and the mirror plane bisecting the



Fig. 2. ORTEP diagram for bis [*N*-methylpiperazinium(+1)trichloroplatinate(II)], [*N*,*N*'-dimethylpiperazinium(+2)] [tetrachloroplatinute(II)] dihydrate, [PtCl₁(H₂Meppz)]₂[H₂Me₂ppz]²⁺ [PtCl₄]²⁻. 2H₂O (2), with the atomic numbering scheme used. The hydrogen bonds are indicated by broken lines. Although the *N*,*N'*-dimethylpiperazinium(+2) cation is disordered, for clarity the figure is drawn including only the C(6) and C(7) atoms whose hydrogen atoms have been obtained by geometrical calculations. The displacement ellipsoids are drawn at the 50% probability level and the selected H atoms are shown as spheres of arbitrary radii.

piperazine ring is 35.7 $(1.7)^{\circ}$ (Table 3). As already observed for complex 1, the H(1)N hydrogen atom is involved in a stabilizing intramolecular hydrogen bond N(1)-H(1)-N…Cl(3) whose distances and angle are N(1)…Cl(3) = 3.02(2) Å and H(1)N…Cl(3) = 2.78(2) Å and N(1)-H(1)N…Cl(3) = 96.4(1.4)°, respectively. The value found for the Cl(3)-Pt(1)-N(1) angle (86.5(4)°) supports the previous finding [1], being smaller than 90°.

The data demonstrate that along the z direction (z perpendicular to the coordination plane of the Pt atom) Pt(1)has two short contacts: $Pt(1)\cdots H(2)N^{1}=3.12(2)$ Å, $Pt(1) \cdots H(4)B^{1} = 3.24(2)$ Å. Pt(2) also has two short contacts: $Pt(2) \cdots H(3)B^{1} = 3.02(3)$ ($^{1}=1/2-x, -1/2+$ $v_1 - z$). Also in this crystal intermolecular N⁺-H···Cl hydrogen bonds are formed: $N(2) \cdots Cl(1)^{t} = 3.21(2) \text{ Å}$ (angle $N(2)-H(2)\cdots Cl(1)^{1} = 151.4(1.7)^{\circ}),$ $N(2) \cdots Cl(2)^{T} =$ 3.39(2) Å (angle N(2)-H(2)···Cl(2)¹ = $127.6(1.6)^{\circ}$); $N(1)\cdots Cl(4)^{1} = 3.36(2) Å$ (angle $N(1)-H(1)\cdots Cl(4)^{1} =$ $169.6(1.6)^{\circ}$, where i = 1/2 - x, 1/2 + y, -z. The water molecule forms a rather strong hydrogen bond with the dipositive piperazinium cation: $N(3)\cdots O(1)W^{II} = 2.75(3)$ Å $(angle N(3)-H(3)\cdots O(1)W'' = 161.2(2.2)^{\circ})('' = 1/2 + x,$ 1/2 - y, 1 + z). Furthermore, the water molecule is weakly hydrogen bonded to the bulky $[PtCl_4]^{2-}$ anion with a distance $Cl(5)\cdots O(1)W^{iii} = 3.13(2) \text{ Å } (^{iii} = -x, -y, -z).$ The stand-alone dipositive cation shows a chair conformation but its disorder does not allow a detailed discussion about molecular dimension. The $[PtCl_4]^{2-}$ anion has normal distances (Pt(2)-Cl(4) = 2.309(7) Å and Pt(2)-Cl(5) =2.296(6) Å) and angle $(Cl(4)-Pt-Cl(5) = 88.8(2)^{\circ})$.

The crystal structure determination of compound 2 shows evidence that the piperazinium ring is coordinated to platinum(II) through a nitrogen atom that has lost its methyl group. This fact is very surprising and, even though kinetic factors cannot be neglected, it is consistent with other findings. No example of platinum(II) coordination through a methylated nitrogen of piperazine ring in chair conformation has yet been reported whereas such a coordination occurs only when the piperazine ing assumes the boat conformation, as found for the complexes cis-[PtCl₂(Me₂ppz)] [1], cis- $[PtCl_3(HMeppz)]$ [27] and trans- $[Pt(HMeppz)_2]^{2+}$ [28] recently synthesized and characterized by us. This behaviour is likely due to steric hindrance between methyl group bound to nitrogen and the cis ligand bound to Pt(II). Such a hindrance is reduced but not removed when piperazine assumes the boat conformation since X-ray structures of the boat piperazine complexes [1,28] show that the methyl groups are still involved in short contacts with the *cis* ligand. In addition, as already discussed [1], the presence of the N-H instead of N-CH₃ group is also favoured by the formation of a strong intramolecular hydrogen bond that further stabilizes the Pt-N bond. Finally the mean single Pt-N bond strength is comparable with that of CH₃-N. The dissociation energy of the Pt-N bond between platinum and the N(7) atom of 9-methyladenine has been found to be 217 kJ mol⁻¹ [29] and the dissociation energy of the CH₃-N bond is slightly

higher ($\Delta H_{\text{diss}} = 285 \text{ kJ mol}^{-1}$) [30]. All these factors make it possible that $-CH_3$ behaves as a leaving group.

3.3.1. Disorder of the stand-alone dipositive piperazinium cation

The piperazinium cation possessing the chair conformation is centrosymmetric and has its molecular centre of symmetry at $(1/2 \ 0 \ 1/2)$. Moreover, this stand-alone dipositive piperazinium cation is disordered but only at the C(6) and C(7)atoms whereas N(3) and C(8) are completely ordered. In fact, the anisotropic refinement indicates very large U_{22} $(0.138-0.292 \text{ Å}^2)$ or U_{33} (0.137 Å²) thermal factors only for C(6) and C(7) and also suggests splitting of these atoms. The refinement was then continued with C(6) and C(7) split in C(6)A and C(6)B and C(7)A and C(7)B, respectively. This model indicates for these atoms very large U_{22} or U_{33} thermal factors (Table 8S, Supplementary material). Then, an isotropic refinement was undertaken with C(6) split again in C(6)A and C(6)B atoms and C(7) split in C(7)A, C(7)B, C(7)C and C(7)D atoms (as suggested by SHELXL 93 [3]) but with different fractional occupancies (Tables 4S and 6S, Supplementary material).

Taking into account that (a) these six atoms differ mainly in y and z coordinates, (b) the U_{22} and U_{33} thermal factors of C(6) and C(7) are very large during the anisotropic refinement, (c) N(3) and C(8) do not suffer of any form of disorder, and (d) the N(3)-C(8) bond is practically positioned along the [10 - 1] axis (having direction cosines: 0.646 (13); 0.091 (24); -0.757 (12)), we can conclude that the disorder is likely due to the rotational motion of the dipositive piperazinium cation, as a rigid group, around the N(3)-C(8) axis.

3.4. Single-crystal structure of [H₂Me₂ ppz]² ' [PtCl₆]² " (3)

Table 4 reports the bond lengths and angles of [N,N']dimethylpiperazinium(+2) hexachloroplatinate(IV)] (3). Systematic extinctions indicated two possible space groups Pnn2 (No. 34) and Pnnm (No. 58); we have used the second space group since it is centrosymmetric. This choice was subsequently confirmed by the final R factor of 0.0217. The structure consists of dipositive N,N'-dimethylpiperazinium(+2) cations, $[C_0H_{10}N_2]^{2+}$ and hexachloroplatinate(IV) anions, $[PtCl_6]^{2-}$, as illustrated in Fig. 3. The dipositive cation possesses a chair conformation as indicated by the endocyclic C-C torsion angle $(57.7(4)^{\circ})$ and by the circumstance that its centre of symmetry coincides with a crystallographic centre of symmetry. The $[PtCl_6]^{2-1}$ anion has the Pt atom on the centre of symmetry at (0, 0, 0), in such a way that each $[PtCl_6]^{2-}$ anion is octahedrally surrounded by six $[C_6H_{16}N_2]^{2+}$ cations and that each $[C_6H_{16}N_2]^{2+}$ cation is octahedrally surrounded by six $[PtCl_{6}]^{2-}$ anions. Moreover, the octahedron is compressed along the *a* axis (i.c. the anion-cation distances are closer) because there is a strong bifurcated hydrogen bond running



Fig. 3. ORTEP diagram for [N,N'-dimethylpiperazinium(+2)] [hexachloroplatinate(IV)], $[H_2Me_2ppz]^{2+}[PtCl_6]^{2-}(3)$ with the atomic numbering scheme used. The displacement ellipsoids are drawn at the 50% probability level and the selected H atoms are shown as spheres of arbitrary radii.

along the *a* axis (see scheme and further details reported in the text).

The endocyclic C-C (1.510(9) Å) and C-N (1.495(5) Å) distances and the exocyclic C-N distance (1.492(8) Å) compare well with the known examples of the dipositive *N*,*N'*-dimethylpiperazinium cation as, for example, in *N*,*N'*-dimethylpiperazinium bis(aqua-trichloro-copper(11)) [31]: C-C = 1.501(9) Å, C-N_{endo} = 1.503(7) Å and C-N_{exo} = 1.523(9) Å or in bis(*N*-methylpiperazinium) *N*-methylpiperazine bis(tetracarbonylcobalt) [32]: C-C = 1.513(8) Å, C-N_{endo} = 1.478(8) Å and C-N_{exo} = 1.480(9) Å.

The [PtCl₆]²⁻ anion is very similar to that found in piperazinium(+2) hexachloroplatinate(IV) [33], in fact the Pt-Cl(1) and Pt-Cl(2) distances found in the present case (2.323(1) and 2.329(2) Å, respectively) are comparable with those already reported (2.320(1) and 2.308(1) Å, respectively). A strong bifurcated hydrogen bond system, running along the *a* axis, connects [PtCl₆]²⁻, {C₆H₁₆N₂]²⁺, [PtCl₆]²⁻, [C₆H₁₆N₂]²⁺ ions. In fact a N-H group positioned on the mirror plane at z=1/2, is linked with two mirrored Cl atoms forming a four-atom cycle of the type:

The geometrical parameters are: N(1)-H(1) = 0.91 Å; $N(1) \cdots Cl(1)^{1} = 3.227(4)$ Å; $N(1)-H(1) \cdots Cl(1)^{1} = 137.2(3)^{\circ}$ $(^{1} = -1/2 + x, 1/2 - y, 1/2 - z)$. The shortest distance between Pt(IV) and hydrogen atom is very long, 3.456(5) Å, which is a consequence of the octahedral coordination geometry at the platinum centre and is thus different from the behaviour observed in Pt(II) piperazine complexes

4. IR spectra

IR measurements of compounds 1-3 in the 400-50 cm⁻¹ region integrate the data observed for Pt(II) piperazine complexes reported in Part I [1] and are partially consistent with the data reported by Ivanova et al. [34] for Pt(II) and Pt(IV) piperazine complexes. The far-IR spectra of neutral N-methylpiperazine and N.N'-dimethylpiperazine display an absorption band at 327s and 359s cm⁻¹, respectively. Fukushima et al. [35,36] assigned these absorption bands to the skeletal deformation of the hexaatomic ring. In the spectra of diprotonated N-methylpiperazinium(+2) and N,N'-dimethylpiperazinium(+2) dichloride such absorption shifts to 364s and 375bm cm⁻¹, respectively. Since in the 400–250 cm⁻¹ region only one broad strong absorption band, centred at 320 cm^{-1} and consisting of more peaks, is detectable for compounds 1-3 it is reasonable to believe that this strong absorption is mainly due to the skeletal deformation of the piperazinium(+2) ring. However, in compound 1, $[H_2Me_2ppz]^{2+}$ [PtCl₄]²⁻⁻, two ν (Pt–Cl) stretching frequencies of the D_{4h} square-planar [PtCl₄]² are detectable at 326s and 294sh cm⁻¹, partially obscured by the broad band at 320 cm⁻¹. In compound 2, $[PiCl_1(H_2Meppz)]_2[H_2Me_{2^*}]$ ppz]²⁺ [PtCl₄]² + 2H₂O, which contains neutral [PtCl₃₊ (H_2Meppz) and $[H_2Me_2ppz]^{2+1}$ $[PtCl_4]^{2n}$, the $\nu(Pt-Cl)$ of the D_{4h} square-planar $[PtCl_4]^{2n}$ anion and of the [PtCl₃N] group is overlapped by the abovementioned broad band at 320 cm⁻¹, whereas a weak band occurs at 267 cm⁻¹ probably due to the ν (Pt-N) stretching vibration of the [PtCl₃(H₂Meppz)] species. Finally, as expected and consistent with the high octahedral symmetry (O_h) of the $[PtCl_0]^{2-}$ anion present in compound 3, only one $\nu(Pt-Cl)$ stretching mode is observed near 325 cm⁻¹ partially masked by the strong piperazinium (+2) ring deformation as already pointed out.

5. Supplementary material

Fractional atomic coordinates and equivalent isotropic displacement coefficients (U_{eq}) , fractional atomic coordinates of H atoms and isotropic displacement coefficients (U_{eo}) , and anisotropic thermal coefficients for compounds 1–3 are deposited as Supplementary Material (Tables 1S–11S).

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