

# Kinetically and Thermodynamically Controlled Formation of Homo- and Heterobinuclear Platinum(II) and Palladium(II) Complexes Supported by Bidentate Triazolopyrimidine Ligands

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The formation of the mononuclear Pt(II) compound *cis*-[Pt(NH<sub>3</sub>)<sub>2</sub>(Hmtpo-*N*<sup>3</sup>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O (**1**) (Hmtpo = 4,7-dihydro-5-methyl-7-oxo[1,2,4]triazolo[1,5-*a*]pyrimidine) upon reaction of Hmtpo with cisplatin is reported. Subsequent reactions of **1** with Pd(II) electrophiles of the type [Pd(am)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> ((am)<sub>2</sub> = en, bpy) in neutral aqueous media afford heterobinuclear complexes of formula [(NH<sub>3</sub>)<sub>2</sub>Pt(μ-mtpo-*N*<sup>3</sup>,*N*<sup>4</sup>)<sub>2</sub>Pd(am)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>, where (am)<sub>2</sub> = bpy (**2**) and en (**3**). On the other hand, reaction of **1** with the platinum electrophile [Pt(bpy)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> yields the binuclear compound [(mtpo-*N*<sup>3</sup>)(NH<sub>3</sub>)<sub>2</sub>Pt(μ-mtpo-*N*<sup>3</sup>,*N*<sup>4</sup>)Pt(bpy)(OH)](NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (**4**). The compounds have been structurally characterized by 1-D and 2-D <sup>1</sup>H NMR spectroscopy and X-ray crystallography (**1**, **2**, and **4**). Compound **1** crystallizes in the triclinic space group *P* $\bar{1}$  with unit cell dimensions *a* = 7.859(1) Å, *b* = 11.811(2) Å, *c* = 12.986(2) Å, α = 73.69(1)°, β = 84.53(1)°, γ = 85.80(1)°, and *Z* = 2. Compound **2** crystallizes in the monoclinic space group *P*2<sub>1</sub>/*c* with unit cell dimensions *a* = 13.752(1) Å, *b* = 12.5658(8) Å, *c* = 19.215(1) Å, β = 118.08(1)°, and *Z* = 4. Compound **4** crystallizes in the triclinic space group *P* $\bar{1}$  with unit cell dimensions *a* = 10.282(2) Å, *b* = 14.133(3) Å, *c* = 14.794(3) Å, α = 110.63(3)°, β = 97.83(3)°, γ = 108.48(3)°, and *Z* = 2. The structure of **1** consists of mononuclear *cis*-[Pt(NH<sub>3</sub>)<sub>2</sub>(Hmtpo-*N*<sup>3</sup>)<sub>2</sub>]<sup>2+</sup> cations, in which the Hmtpo ligands are coordinated through N(3) in a monodentate fashion. In compound **2**, two mtpo moieties bridge the metal centers through N(3) and N(4), giving rise to a Pt–Pd separation of 3.083(1) Å. On the other hand, only one bridging mtpo moiety is present in **4**, which accounts for a lengthening in the M–M separation to 3.337(1) Å. The environment around the metal centers consists of four nitrogens, except for one Pt nucleus in compound **4**, which presents a rare example of a terminal OH group. The <sup>1</sup>H NMR studies show clearly that these structures are retained in solution. Finally, a bidentate bridging mode through N(1)/N(3) is postulated for the species generated in solution by the reaction of **1** with the electrophile [Pt(NH<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup>, which may lead to tetranuclear or polymeric species.

## Introduction

Direct metal–metal interaction in dimeric and polymeric platinum(II) compounds is a subject of current interest. Such species can be formed from reaction of the anticancer drug cisplatin<sup>1</sup> with different amidate ligands and related compounds.<sup>2</sup> The association of platinum units to form dimers appears also to be a key step in the formation of the “platinum blues”.<sup>3</sup> Furthermore, there is also interest in the formation of Pd(II) analogues,<sup>4</sup> which are more difficult to oxidize, although mixed-valence compounds have been reported in a few cases.<sup>5</sup>

In a previous paper,<sup>6</sup> we reported the synthesis, structural characterization, and study on the nature of the Pt···Pt interaction in the binuclear complex [Pt<sub>2</sub>(μ-mtpo-*N*<sup>3</sup>,*N*<sup>4</sup>)<sub>4</sub>] (mtpo = 4,7-dihydro-5-methyl-7-oxo[1,2,4]triazolo[1,5-*a*]pyrimidine), which is formed upon condensation of two *cis*-[PtCl<sub>2</sub>(Hmtpo-*N*<sup>3</sup>)<sub>2</sub>] monomers. The presence of four bridging mtpo moieties in this complex gives rise to a very short Pt–Pt contact, of 2.744(2) Å. However, in spite of its short intermetallic separation, this compound was found to be inert toward oxidation to a mixed-valence compound. This fact has been attributed to the steric effect of the methyl group of the mtpo moieties, which appears to prevent nucleophiles or electrophiles from approaching the metal centers, hence hindering the oxidation process.

In this paper, we report the reactivity of the mononuclear compound *cis*-[Pt(NH<sub>3</sub>)<sub>2</sub>(Hmtpo-*N*<sup>3</sup>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O (**1**) toward *cis*-[M(am)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> electrophiles (M = Pt(II), Pd(II); (am)<sub>2</sub> = (NH<sub>3</sub>)<sub>2</sub>, en, bpy) with the goal of obtaining binuclear complexes of formula [Pt(NH<sub>3</sub>)<sub>2</sub>(mtpo-*N*<sup>3</sup>,*N*<sup>4</sup>)<sub>2</sub>M(am)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> (see Scheme 1). These compounds were initially thought to be more sterically oxidizable than the previously described Pt<sub>2</sub>-(mtpo-*N*<sup>3</sup>,*N*<sup>4</sup>)<sub>4</sub><sup>6</sup> and could eventually be used as precursors for mixed-valence oligomers. The reaction of **1** with Pd(II) electrophiles yields the expected binuclear products. However, the slower kinetics of Pt(II) appears to be responsible for a more complex reactivity. Thus, the reaction of **1** with [Pt(am)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]-

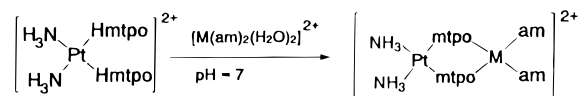
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## Scheme 1



(NO<sub>3</sub>)<sub>2</sub> ((am)<sub>2</sub> = (NH<sub>3</sub>)<sub>2</sub>, bpy) yields the binuclear compound [(mtpo-*N*<sup>3</sup>)(NH<sub>3</sub>)<sub>2</sub>Pt(mtpo-*N*<sup>3</sup>,*N*<sup>4</sup>)Pt(bpy)(OH)] NO<sub>3</sub> and a species that could not be isolated, for which the cyclic tetranuclear structure [Pt<sub>4</sub>(NH<sub>3</sub>)<sub>8</sub>(mtpo-*N*<sup>1</sup>,*N*<sup>3</sup>)<sub>4</sub>]<sup>4+</sup> is proposed.

## Experimental Section

**Reactants and Methods.** *cis*-[PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] was purchased from Aldrich Chemical Co. or prepared by a modification of Dhara's method.<sup>7</sup> [PtCl<sub>2</sub>(bpy)],<sup>8</sup> [PdCl<sub>2</sub>(bpy)], and [PdCl<sub>2</sub>(en)]<sup>9</sup> (bpy = 2,2'-bipyridine; en = ethylenediamine) were prepared by standard literature methods and transformed to their respective aquated species by treatment with AgNO<sub>3</sub> in the dark. 4,7-Dihydro-5-methyl-7-oxo[1,2,4]-triazolo[1,5-*a*]pyrimidine was purchased from Aldrich Chemical Co. and used as received. The other chemical reagents and solvents were obtained from commercial sources. All experiments were performed in air.

**Preparation of [Pt(NH<sub>3</sub>)<sub>2</sub>(Hmtpo)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O, 1.** A solution of Hmtpo (4 mmol in ca. 25 mL of water) was mixed with a solution containing *cis*-[Pt(NH<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> (2 mmol in ca. 10 mL of water). The resulting colorless solution was kept at 40 °C for 4 days, in order to ensure complete reaction. The solution was then concentrated to 10 mL, giving a precipitate of colorless crystals, which were rinsed with a small amount of water and air-dried. A smaller fraction of crystals was recovered in the following 2 days. Yield: 57%. Anal. Calcd (found) for C<sub>12</sub>H<sub>22</sub>N<sub>12</sub>O<sub>10</sub>Pt: C, 20.9 (20.8); H, 3.2 (3.3); N, 24.4 (24.3); Pt, 28.3 (28.9). IR (selected bands in cm<sup>-1</sup>): 1385 vs, 1535 s, 1585 vs, 1640 vs, 1720 vs, 3250 s, 3405 s.

**Preparation of [Pt(NH<sub>3</sub>)<sub>2</sub>(μ-mtpo)<sub>2</sub>Pd(bpy)](NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, 2.** To an aqueous solution of **1** (0.500 mmol in ca. 10 mL) was added a warm solution of [Pd(bpy)(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> (0.500 mmol in ca. 20 mL of water), after which the pH was adjusted to 7.5 with 1 N NaOH. The resulting orange solution was kept at 45 °C for 48 h in order to complete the reaction. Subsequent concentration of the solution gave yellow crystals of **2**, which were washed with water. The compound slowly alters on exposure to air. Yield: 46%. Anal. Calcd (found) for C<sub>22</sub>H<sub>30</sub>N<sub>14</sub>O<sub>11</sub>PtPd: C, 27.3 (27.1); H, 3.1 (2.7); N, 20.2 (20.4). IR (cm<sup>-1</sup>): 770 m, 830 m, 1385 vs, 1420 s, 1540 vs, 1590 m, 1680 vs, 3250 s, 3420 s.

**Preparation of [Pt(NH<sub>3</sub>)<sub>2</sub>(μ-mtpo)<sub>2</sub>Pd(en)](NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O, 3.** This complex was prepared using the procedure described above for **2**. In this case, yellow crystals of **3** were obtained, which also alter slowly on exposure to air. Yield: 47%. Anal. Calcd (found) for C<sub>14</sub>H<sub>28</sub>N<sub>14</sub>O<sub>10</sub>PtPd: C, 18.0 (18.1); H, 3.6 (3.9); N, 21.2 (20.8). IR (selected bands in cm<sup>-1</sup>): 1385 vs, 1420 s, 1535 vs, 1590 m, 1675 vs, 3215 s, 3440 s.

**Preparation of [(mtpo)(NH<sub>3</sub>)<sub>2</sub>Pt(μ-mtpo)Pt(bpy)(OH)](NO<sub>3</sub>)·6H<sub>2</sub>O, 4.** The mixture of a warm aqueous solution of [Pt(bpy)(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> (0.666 mmol in ca. 80 mL) with a solution of **1** (0.666 mmol in ca. 10 mL of water) and subsequent neutralization with NaOH (1 N) gave an orange-red suspension. The resulting reaction mixture was stirred at 50 °C for 24 h and then filtered to eliminate unreacted starting materials. The subsequent concentration to 4 mL, followed by filtration, gave a red solution which produced a small amount of extremely air-sensitive orange-red crystals. X-ray-quality crystals of **4** were obtained by slowly lowering the temperature of a 60 °C aqueous solution of **4** (14 mg in 0.5 mL). Yield: 4%. Subsequent attempts to improve the yield of the reaction were fruitless. Anal. Calcd (found) for C<sub>22</sub>H<sub>37</sub>N<sub>13</sub>O<sub>12</sub>Pt<sub>2</sub>: C, 24.8 (24.4); H, 3.5 (3.5); N, 17.1 (17.1). IR (selected bands in cm<sup>-1</sup>): 765 m, 820 m, 1350 s, 1385 vs, 1422 s, 1524 vs, 1545 vs, 1650 vs, 1665 vs, 1680 vs, 3430 s.

**Instrumentation.** Elemental analyses for C, H, and N were performed on a Fisons-Instruments EA-1008 at the Instrumentation

Center of the University of Granada. Infrared spectra were recorded in the 4000–180 cm<sup>-1</sup> range on a Perkin-Elmer 983G spectrophotometer, using KBr and polyethylene pellets. TG diagrams were obtained on a Mettler TA-3000 instrument equipped with a Mettler TG-50 thermobalance at a heating rate of 20 K min<sup>-1</sup>, using an atmosphere of pure air (100 mL min<sup>-1</sup>). 1-D and 2-D <sup>1</sup>H NMR spectra were recorded in D<sub>2</sub>O with TSP as internal standard on a Bruker AM-300 FT NMR spectrometer at the Instrumentation Center of the University of Granada.

**X-ray Crystallography.** Relevant crystallographic data and details of refinement for compounds **1**, **2**, and **4** are presented in Table 1. The crystals were mounted on a Stoe-Siemens STADI-4 diffractometer. In the case of **4**, it was necessary to seal the crystals in a Lindemann capillary with a few drops of the mother liquor. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction ( $\psi$  scans) was applied. The structures were solved by heavy-atom and Fourier methods using the SHELXTL PLUS program package.<sup>10</sup> Full-matrix least-squares refinement on *F* was performed. Non-hydrogen atoms were described with anisotropic thermal parameters. In the case of compounds **1** and **4**, the final refinements were performed on *F*<sup>2</sup> by means of the SHELX-93 program.<sup>11</sup>

Compounds **1** and **4** showed disorder involving a nitrate anion and an interstitial water molecule. The disorder was modeled by considering two positions for each of these groups, with subsequent refinement of occupancy factors.

## Results and Discussion

The reaction of *cis*-[Pt(NH<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> with Hmtpo in a 1:2 ratio yielded the mononuclear compound *cis*-[Pt(NH<sub>3</sub>)<sub>2</sub>(Hmtpo-*N*<sup>3</sup>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O (**1**), which was used as precursor for the preparation of the subsequent binuclear compounds.

**Structure of *cis*-[Pt(NH<sub>3</sub>)<sub>2</sub>(Hmtpo-*N*<sup>3</sup>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O (**1**).** The structure is composed of mononuclear *cis*-[Pt(NH<sub>3</sub>)<sub>2</sub>(Hmtpo-*N*<sup>3</sup>)<sub>2</sub>]<sup>2+</sup> cations, nitrate anions, and two crystallization water molecules. The cation of **1** is depicted in Figure 1, and selected interatomic distances and angles are presented in Table 2. The four nitrogen ligands adopt a nearly ideal square planar geometry about the platinum atom (±0.05 Å), with the ligands in a *cis* configuration, which is consistent with the preparation method, binding of Hmtpo taking place via N(3). The Pt–N bond distances compare well with those found in the literature for cisplatin complexes with similar heterocyclic ligands such as nucleobases.<sup>12</sup>

The Hmtpo ligands dispose in a *head to tail* orientation which is the most usual feature found in cisplatin adducts with similar heterocyclic ligands.<sup>13</sup> However, it should be noted that the substitution of the NH<sub>3</sub> groups by chlorine ligands, together with the formation of a water bridge via hydrogen bonding between the two Hmtpo ligands in *cis*-[PtCl<sub>2</sub>(Hmtpo-*N*<sup>3</sup>)<sub>2</sub>]<sup>2+</sup>·2H<sub>2</sub>O,<sup>14</sup> leads to the stabilization, in the solid state, of the corresponding *head to head* atropisomer. This observation shows that small energetic contributions such as those due to hydrogen bonding or crystal packing may lead to the stabilization of different atropisomers,<sup>15,16</sup> so the energy difference between them must be likewise small.

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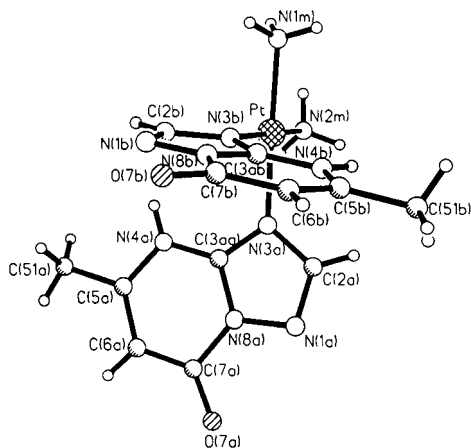
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**Table 1.** Crystallographic Data and Details of Refinement

|  | 1  | 2   | 4   |
|--|--|---|---|
| formula  | C <sub>12</sub> H <sub>22</sub> N <sub>12</sub> O <sub>10</sub> Pt | C <sub>22</sub> H <sub>26</sub> N <sub>14</sub> O <sub>9</sub> PdPt | C <sub>22</sub> H <sub>37</sub> N <sub>13</sub> O <sub>12</sub> Pt <sub>2</sub> |
| fw   | 689.51   | 932.1   | 1065.83   |
| crystal system   | triclinic  | monoclinic  | triclinic   |
| space group  | <i>P</i> $\bar{1}$   | <i>P</i> <sub>2</sub> / <i>c</i>                                    | <i>P</i> $\bar{1}$  |
| <i>a</i> , Å   | 7.859(1)   | 13.752(2)   | 10.282(2)   |
| <i>b</i> , Å   | 11.811(2)  | 12.566(2)   | 14.133(3)   |
| <i>c</i> , Å   | 12.986(2)  | 19.215(2)   | 14.794(3)   |
| $\alpha$ , deg   | 73.69(1)   | 90  | 110.63(3)   |
| $\beta$ , deg  | 84.53(1)   | 118.08(2)   | 97.83(3)  |
| $\gamma$ , deg   | 85.80(1)   | 90  | 108.48(3)   |
| <i>V</i> , Å <sup>3</sup>  | 1150.3(3)  | 2929.5(7)   | 1832.3(6)   |
| <i>Z</i>   | 2  | 4   | 2   |
| crystal size, mm   | 0.2 × 0.15 × 0.1   | 0.3 × 0.2 × 0.15  | 0.3 × 0.1 × 0.1   |
| <i>d</i> <sub>calc</sub> , g/cm <sup>3</sup>                               | 1.991  | 2.113   | 1.932   |
| $\lambda$ (Mo K $\alpha$ ), Å  | 0.710 73   | 0.710 73  | 0.710 73  |
| $\mu$ <sub>MoK<math>\alpha</math></sub> , cm <sup>-1</sup>                 | 62   | 55  | 77  |
| <i>F</i> (000)   | 672  | 1808  | 1024  |
| scan   | 2 $\theta$ / $\omega$  | 2 $\theta$ / $\omega$   | 2 $\theta$ / $\omega$   |
| no. of measd reflns  | 4347   | 6756  | 7517  |
| no. of indep reflns ( <i>R</i> <sub>int</sub> , %)                         | 4028 (2.45)  | 5152 (3.05)   | 5666 (4.66)   |
| no. of obs reflns ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))                    |  | 4134  |   |
| <i>R</i> <sub>w</sub> <sup>a</sup> % ( <i>I</i> > 2 $\sigma$ ( <i>I</i> )) | 5.02   | 2.95  | 5.06  |
| <i>R</i> <sub>w</sub> <sup>b</sup> % ( <i>I</i> > 2 $\sigma$ ( <i>I</i> )) |  | 3.21  |   |
| <i>R</i> <sub>w2</sub> <sup>c</sup> % (all data)                           | 14.32  |   | 16.06   |
| goodness-of-fit  | 1.19   | 1.04  | 1.10  |
| largest diff peak and hole, e <sup>-</sup> Å <sup>-3</sup>                 | 2.125 and -2.630   | 1.11 and -0.69  | 1.55 and -1.97  |
| no. of params refined  | 311  | 425   | 437   |

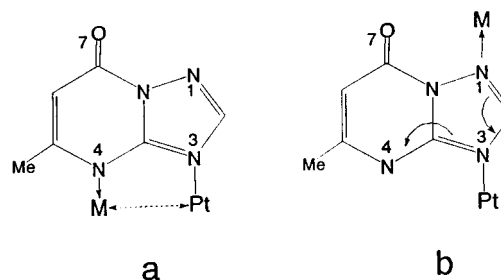
<sup>a</sup>  $R = \sum(|F_o| - |F_c|) / \sum|F_o|$ . <sup>b</sup>  $R_w = \sum(|F_o| - |F_c|w^{1/2}) / \sum(|F_o|w^{1/2})$ , where  $w = (\sigma^2(F) + 0.0008F^2)^{-1}$ . <sup>c</sup>  $R_{w2} = [\sum w(F_o^2 - F_c^2)^2 / \sum (wF_o^4)]^{1/2}$ , where  $w = [\sigma^2(F_o)^2 + (0.060P)^2]^{-1}$  for compound **1**,  $w = [\sigma^2(F_o)^2 + (0.1045P)^2 + 3.2202P]^{-1}$  for compound **4**, and  $P = (F_o^2 + 2F_c^2)/3$ .

**Figure 1.** Geometry of the cation [Pt(NH<sub>3</sub>)<sub>2</sub>(Hmtpo-*N*<sup>3</sup>)<sub>2</sub>]<sup>2+</sup> in **1**.**Table 2.** Selected Bond Lengths and Angles for **1**

| Bond Distances, Å          |          |                |          |
|----------------------------|----------|----------------|----------|
| Pt–N(1M)                   | 2.003(9) | Pt–N(3A)       | 2.012(8) |
| Pt–N(3B)                   | 2.018(8) | Pt–N(2M)       | 2.035(8) |
| Hydrogen Bond Distances, Å |          |                |          |
| N(4B)–O(1W)                | 2.706    | N(1M)–O(3N)    | 2.964    |
| N(2M)–O(1N)                | 3.007    |                |          |
| Bond Angles, deg           |          |                |          |
| N(1M)–Pt–N(3A)             | 176.6(3) | N(1M)–Pt–N(3B) | 90.6(3)  |
| N(3A)–Pt–N(3B)             | 88.0(3)  | N(1M)–Pt–N(2M) | 90.7(3)  |
| N(3A)–Pt–N(2M)             | 90.9(3)  | N(3B)–Pt–N(2M) | 176.3(3) |
| Pt–N(3A)–C(3A)             | 127.0(6) | Pt–N(3B)–C(3A) | 129.5(7) |

In the crystal, the cations associate in pairs by means of the stacking interactions that take place between their Hmtpo rings labeled “A” (3.27 Å separating the corresponding average planes) and a weak hydrogen bond of 3.083 Å between N(1M) and O(7A) [ $-x + 1, -y, -z$ ].

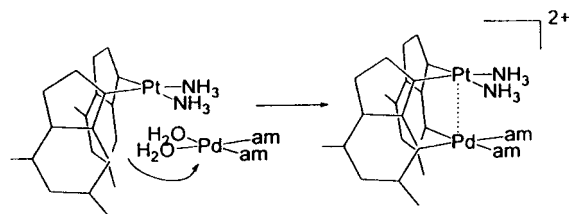
### Reactivity of *cis*-[Pt(NH<sub>3</sub>)<sub>2</sub>(Hmtpo-*N*<sup>3</sup>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> toward Platinum and Palladium Electrophiles of the Cisplatin Type.

**Chart 1**

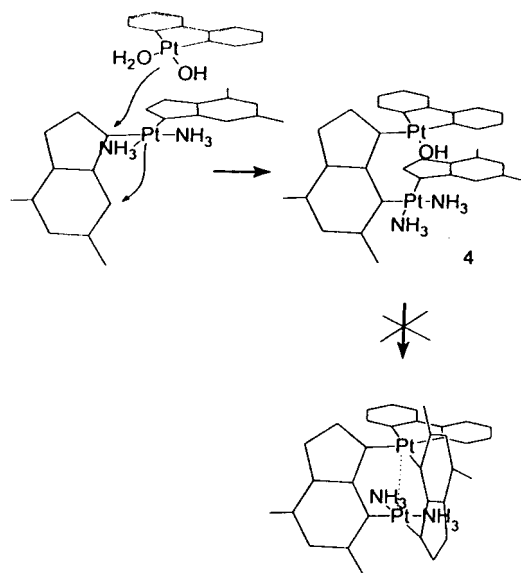
The *cis*-[Pt(NH<sub>3</sub>)<sub>2</sub>(Hmtpo-*N*<sup>3</sup>)<sub>2</sub>]<sup>2+</sup> (**1**) species offers the possibility of behaving as a donor ligand toward metal ions, since it provides three available binding sites at N(1), O(7), and N(4), after deprotonation of the last (p*K*<sub>a</sub> = 6.3 for free Hmtpo). However, the soft natures of Pt(II) and Pd(II) ions make the ring nitrogens more suitable as binding sites for these metals in neutral aqueous media (see Chart 1). The metal ion coordinates preferentially to N(4), because N(4) is more basic than N(1), which is consistent with N(4)–H being the most stable tautomeric form of Hmtpo.<sup>17</sup> Thus, the reaction of **1** with [Pd(am)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> electrophiles ((am)<sub>2</sub> = bpy, en) leads to the formation, after metal attack on N(4) nitrogens, of heterobinuclear complexes of formula [(NH<sub>3</sub>)<sub>2</sub>Pt(*μ*-mtpo-*N*<sup>3</sup>,*N*<sup>4</sup>)<sub>2</sub>-Pd(am)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> ((am)<sub>2</sub> = bpy (**2**), en (**3**)), in which two mtpo moieties bridge the metal centers (see Scheme 2). The structure of **2** has been solved by X-ray methods and will be discussed later.

Our attempts to synthesize the [(NH<sub>3</sub>)<sub>2</sub>Pt(*μ*-mtpo-*N*<sup>3</sup>,*N*<sup>4</sup>)<sub>2</sub>Pt(am)<sub>2</sub>]<sup>2+</sup> complexes, which could be regarded as suitable starting materials for the formation of the platinum blues, have been unsuccessful so far, which may be due to the slower kinetics of Pt(II) compared to Pd(II). Thus, the reaction of **1** with [Pt-(bpy)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> does not result in the formation of a binuclear species analogous to the above mentioned mixed Pt–Pd

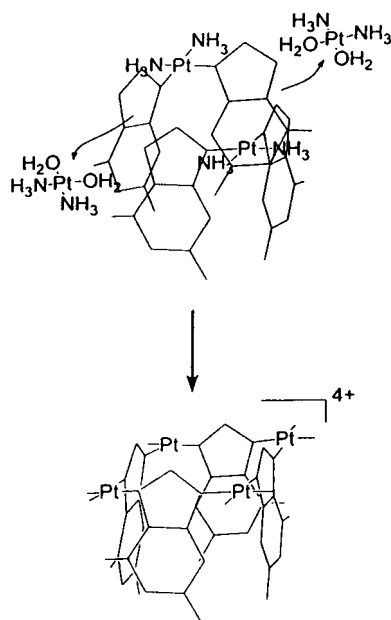
## Scheme 2



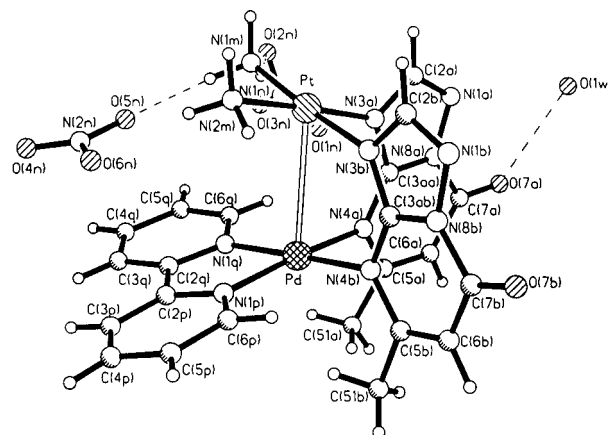
## Scheme 3



## Scheme 4



binuclear compound, but it appears that the reaction stops before completion, yielding compound **4** (see Scheme 3). **4** is a binuclear compound in which only one mtpo moiety bridges the two platinum centers, the structure of which will be discussed subsequently. Furthermore, the monitoring of the reaction of **1** with  $cis\text{-}[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2]^{2+}$  by  $^1\text{H}$  NMR spectroscopy shows that the second platinum center clearly does not bind to N(4), as found in the previous cases, but possibly to N(1), which may lead to the formation of polymeric or cyclic species (see Scheme 4) as a result of the bridging coordination of the mtpo moieties through N(1)/N(3) (*vide infra*).



**Figure 2.** Molecular structure and labeling of  $cis\text{-}[\text{Pt}(\text{NH}_3)_2(\mu\text{-mtpo-}N^3,N^4)_2\text{Pd}(\text{bpy})](\text{NO}_3)_2$  (**2**).

**Table 3.** Selected Bond Lengths and Angles for **2**

| Bond Distances, Å          |          |                           |          |
|----------------------------|----------|---------------------------|----------|
| Pt–Pd                      | 3.083(1) | Pt–N(1M)                  | 2.034(6) |
| Pt–N(2M)                   | 2.032(7) | Pt–N(3A)                  | 2.018(6) |
| Pt–N(3B)                   | 2.006(5) | Pd–N(1P)                  | 2.011(5) |
| Pd–N(1Q)                   | 2.014(5) | Pd–N(4A)                  | 2.064(5) |
| Pd–N(4B)                   | 2.054(5) |                           |          |
| Hydrogen Bond Distances, Å |          |                           |          |
| N(1M)–O(5N)                | 2.930(9) | N(2M)–O(2N) <sup>ii</sup> | 2.979(9) |
| N(1M)–O(2N)                | 2.958(9) | O(1W)–O(7A)               | 2.852(9) |
| N(2M)–O(7B) <sup>i</sup>   | 2.922(9) |                           |          |
| Bond Angles, deg           |          |                           |          |
| N(1M)–Pt–N(2M)             | 91.7(3)  | N(1M)–Pt–N(3A)            | 89.8(2)  |
| N(2M)–Pt–N(3A)             | 178.0(2) | N(1M)–Pt–N(3B)            | 175.8(2) |
| N(2M)–Pt–N(3B)             | 88.5(2)  | N(3A)–Pt–N(3B)            | 90.1(2)  |
| N(1P)–Pd–N(1Q)             | 80.7(2)  | N(1P)–Pd–N(4A)            | 172.2(2) |
| N(1Q)–Pd–N(4A)             | 94.8(2)  | N(1P)–Pd–N(4B)            | 94.3(2)  |
| N(1Q)–Pd–N(4B)             | 174.8(2) | N(4A)–Pd–N(4B)            | 90.3(2)  |
| Pt–N(3A)–C(3aA)            | 126.3(4) | Pt–N(3B)–C(3aB)           | 130.9(3) |
| Pd–N(4A)–C(3aA)            | 122.1(4) | Pd–N(4B)–C(3aB)           | 118.4(4) |

<sup>a</sup> Symmetry relations: (i)  $-x, -y + 1, -z$ ; (ii)  $-x, y + 0.5, -z + 0.5$ .

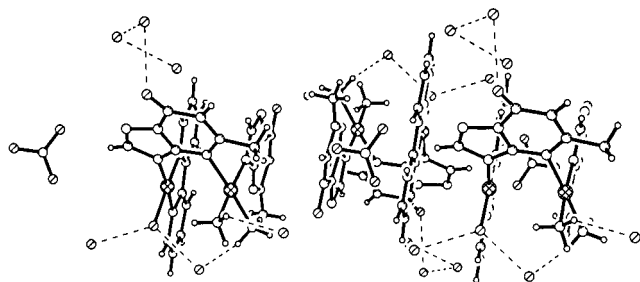
**Crystal Structure of  $cis\text{-}[\text{Pt}(\text{NH}_3)_2(\mu\text{-mtpo-}N^3,N^4)_2\text{Pd}(\text{bpy})](\text{NO}_3)_2$  (**2**).** The crystal structure of **2** is shown in Figure 2. A selection of interatomic distances and angles is listed in Table 3. The structure consists of binuclear  $cis\text{-}[\text{Pt}(\text{NH}_3)_2(\mu\text{-mtpo-}N^3,N^4)_2\text{Pd}(\text{bpy})]^{2+}$  cations, uncoordinated nitrate anions, and a water molecule of crystallization. In the binuclear cation, two mtpo moieties bridge the two metal centers, giving rise to a Pt...Pd separation of 3.083(1) Å, which is 0.3 Å shorter than the van der Waals radii sum.<sup>18</sup> This value is in the same range as the distances found for other similar doubly bridged  $d^8$  metal complexes,<sup>19</sup> although considerably longer than that found in the tetrabridged compound  $\text{Pt}_2(\mu\text{-mtpo-}N^3,N^4)_4$ <sup>6</sup> (Pt...Pt 2.744(2) Å).

The Pt atom is coordinated to two N(3) sites of the mtpo ligand and to two  $\text{NH}_3$  groups, whereas the Pd atom is bound to a bpy ligand and the two mtpo moieties via N(4). Palladium binding to N(4) nitrogens is responsible for the *head to head* orientation exhibited by the mtpo moieties (dihedral angle 89.7°). The coordination geometry about the metal centers is square planar with respective deviations of 0.02 and 0.04 Å for Pt and Pd toward each other. The coordination planes are tilted by 29.5° and minimally twisted about the Pt–Pd vector (torsion

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**Figure 4.** Packing of the binuclear units of **4** along the crystallographic *b* axis, as results of  $\pi$ - $\pi$  interactions of bpy and mtpo ligands.

of **4** is stabilized by intermolecular  $\pi$ - $\pi$  interactions between the mtpo rings noted as B (separation of 3.60 Å) and the bpy rings (separation of 3.54 Å), which gives rise to a strand along the *b* axis (see Figure 4). In contrast to the case of **2**, binding of the Pt(OH)(bpy) entity to N(3) allows stacking interactions between the bpy rings.

**M-M Bonding in Complexes 2 and 4.** With respect to the presence of direct metal-metal interactions in compounds **2** and **4**, which show intermetallic distances in the range 3.0–3.3 Å, the literature is still ambiguous. While some authors regard these contacts as nonbonding in nature,<sup>27</sup> others consider them as direct intermetallic bonding interactions, from X-ray crystallography,<sup>28</sup> Raman,<sup>29</sup> and MO *ab initio* studies,<sup>30</sup> or solution behavior.<sup>31</sup> The thesis of direct metal-metal bonding interactions, however, appears to have stronger support.

The electronic nature of the participating ligands may have an important role stabilizing such axial interaction. Thus, Natile and co-workers<sup>28</sup> conclude that the participation in the coordination of ligands with empty  $\pi^*$  orbitals may draw charge from the filled  $d_z^2$  orbitals of the metals and so stabilize the interaction between the two metal units. Thus, the presence of strong  $\pi$  acidic ligands such as bpy and the mtpO moieties with empty  $\pi^*$  orbitals in compounds **2** and **4** may contribute to the stabilization of a favorable metal-metal interaction.

It should be noted that the displacement of the metal centers from the square planar geometry in compounds **2** and **4** occurs always in the direction of the other nucleus (see above). This observation is consistent with the presence of an attractive interaction between both nuclei.<sup>30,32</sup> The final geometry of the molecule must be, however, the result of a mixture of steric demands of the bridging mtpo ligands, interligand interactions in the adjacent coordination planes, and M-M bonding interactions.

**<sup>1</sup>H NMR Studies.** The <sup>1</sup>H NMR data of the studied complexes are summarized in Table 5. <sup>1</sup>H NMR data are very sensitive to the nature of the complex and are therefore of great structural value. Thus, Pt coordination to N(3) in **1** is responsible for a general downfield shift in the signals of the Hmtpo moiety, namely Me (+0.05 ppm), H(6) (+0.12 ppm), and H(2) (+0.24 ppm), this effect being more significative for the last because of the proximity of H(2) to the Pt nucleus. Subsequent coordination of an additional metal to N(4) in compounds **2–4** (ring A) is responsible for an additional

**Table 5.** <sup>1</sup>H NMR Data for the Complexes

| Compounds         | Hmtpo                          |              |              | Auxiliary ligands              |                          |                          |                    |
|-------------------|--------------------------------|--------------|--------------|--------------------------------|--------------------------|--------------------------|--------------------|
|                   | Me                             | H6           | H2           |                                |                          |                          |                    |
| Hmtpo, pD 5.5     | 2.46                           | 5.98         | 8.20         |                                |                          |                          |                    |
| <b>1</b> , pD 2.7 | 2.51                           | 6.10         | 8.44         |                                |                          |                          |                    |
| <b>2</b> , pD 7.6 | 3.12                           | 6.13         | 8.52         | H3<br>8.56                     | bpy<br>H4<br>8.44        | H5<br>7.66               | H6<br>7.73         |
| <b>3</b> , pD 7.8 | 3.10                           | 6.32         | 8.53         |                                | en<br>3.01               |                          |                    |
| <b>4</b> , pD 8.2 | ring<br>A<br>3.17<br>B<br>1.89 | 6.49<br>5.83 | 8.66<br>7.50 | ring<br>Q<br>8.38<br>P<br>7.99 | H3<br>8.38<br>H4<br>8.48 | H5<br>7.94<br>H6<br>7.31 | H6<br>9.46<br>7.31 |
| <b>5</b> , pD 5.0 | 2.52                           | 6.12         | 8.34         |                                |                          |                          |                    |

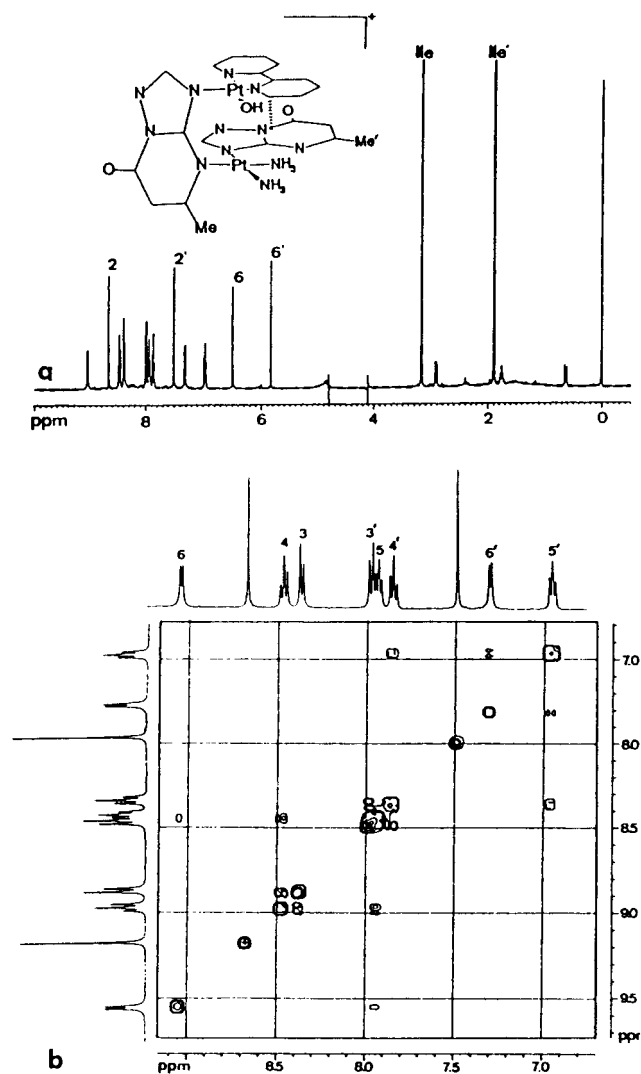
downfield shift in the H(2) resonance (+0.08, +0.09, and +0.22 ppm, respectively, for **2–4**) and the H(6) resonance (+0.03, +0.22, and +0.36 ppm) and a pronounced downfield shift for the methyl group (+0.61, +0.59, and +0.66 ppm) compared to the case of the monomer. The large downfield shift for the methyl groups is a consequence of its location over the metal coordination plane following metal binding to N(4). This observation is diagnostic of involvement of N(4) in the coordination of a  $d^8$  ion.<sup>6</sup> It can also be indicative of a weak  $M\cdots H$  interaction<sup>33</sup> ( $M-H$  separation about 2.6 Å), which can be described as a three-center four-electron  $M\cdots H-C$  interaction,<sup>27</sup> in contrast to the known three-center two-electron agostic interactions.

On the other hand, addition of  $[Pt(NH_3)_2(H_2O)_2]^{2+}$  to a solution of **1** is responsible for an initially very complex spectrum which evolves (after 24 h) to a single set of signals (**5**). In this last case, only a small upfield shift of H(2) (−0.10 ppm) is observed, compared to the case of the precursor compound **1**. We propose that coordination of the second platinum center takes place through N(1), resulting in a bidentate bridging mode through N(1)/N(3) for mtpo, which may give rise to the formation of polynuclear species. From model building, we postulate the possible formation of the cyclic tetranuclear cation  $[Pt_4(NH_3)_8(\mu\text{-mtpo-}N^1, N^3)_4]^{4+}$  (see Scheme 4), similar to  $[(en)Pt(uracilate)]_4^{4+}$ , which was recently reported by Rauter *et al.*<sup>34</sup> Thus, the similarity of the mtpo- $N^1, N^3$  bridge to that of uracilate- $N^1, N^3$  may lead to a similar polynuclear complex. However, in our case, such a compound appears to be difficult to isolate in the solid state, since concentration of the solutions yields syrups difficult to characterize.

For complexes **2–4**, additional signals are present in the <sup>1</sup>H NMR spectra that are attributed to the presence of auxiliary ligands, and for compound **4**, there is a signal attributable to a second mtpo ligand coordinated through N(3) in a monodentate mode (mtpo noted as B). The <sup>1</sup>H NMR spectrum of **2** in the bpy region indicates the equivalence of the two pyridine rings, showing the equivalence of the two arms of the binuclear complex in solution. However, the <sup>1</sup>H NMR spectrum of **4** is more complex (see Figure 5), since four different sets of signals are present (rings A and B of mtpo and pyridine rings P and Q of bpy). The <sup>1</sup>H-<sup>1</sup>H COSY spectrum enabled us to propose <sup>1</sup>H assignments for the bpy ligand (see Figure 5b). The presence of two sets of signals for the bpy ligand shows the inequivalence of the two pyridine rings. Moreover, the signals corresponding to one pyridine ring appear considerably shifted upfield (see Figure 5b) due to the stacking interaction with the mtpo B ring.

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**Figure 5.**  $^1\text{H}$  NMR spectrum (300 MHz,  $\text{D}_2\text{O}$ ,  $\text{pD} = 8.2$ ) (a) and  $^1\text{H}$ – $^1\text{H}$  COSY in the bpy proton region (b) of **4**. The protons corresponding to the two different mtpo rings appear assigned in (a) (primed signals correspond to ring B). In (b) the primed signals correspond to ring P.

On the other hand, there are also two sets of signals associated with the presence of the two inequivalent mtpo moieties. One set corresponds to a mtpo ligand acting in a bidentate bridging mode through N(3)/N(4) (mentioned above) and another set of signals shifted upfield, attributed to the presence of the mtpo coordinated via N(3) in a monodentate fashion. The pronounced upfield shift in the mtpo (B) signals (H(2),  $-0.94$ ; H(6),  $-0.27$ ;

Me,  $-0.62$  ppm) is indicative of the strong stacking interaction with the adjacent bpy ligand. Hence, it can be concluded that the overall solid-state structure is retained in solution.

Finally,  $^1\text{H}$  NMR was used to investigate the possibility of forming a doubly bridged head to tail binuclear species of the type  $[(\text{NH}_3)_2\text{Pt}(\mu\text{-mtpo-}N^3,N^4)_2\text{Pt}(\text{bpy})]^{2+}$  by a rearrangement of the mtpo ligands in **4** (see Scheme 3). However, attempts to achieve this reaction using higher temperatures (up to  $80\text{ }^\circ\text{C}$ ) and lower pH (in order to convert the inert OH ligand in a labile  $\text{H}_2\text{O}$  group with the aim of facilitating its substitution by N(4) from mtpo (B)) were unsuccessful. We conclude that the strong stacking interaction between the bpy and mtpo rings and the steric hindrances may be responsible for the inertness of **4** toward this rearrangement reaction.

## Conclusions

We have shown the coordination versatility of the Hmtpo ligand in the synthesis of polynuclear  $d^8$  metal complexes. The formation of binuclear compounds upon actuation of the ligand in a bridging mode through N(3)/N(4) appears to be thermodynamically favored, whereas the possible formation of cyclic species upon actuation of the ligand in a bridging mode through N(1)/N(3) appears to be kinetically favored.

The  $\text{M}\cdots\text{M}$  separation in the binuclear species seems to be modulated by the number of mtpo bridges, which leads to intermetallic distances ranging from  $2.744(2)\text{ \AA}$  for the tetra-bridged  $\text{Pt}_2(\mu\text{-mtpo})_4$  to  $3.337(1)\text{ \AA}$  for the monobridged **4**. The final geometry of the complexes must be the result of a mixture of steric demands and electronic nature of the bridging ligands, interligand interactions in the adjacent coordination planes, and M–M bonding interactions.

Compound **4** may be considered as an intermediate species in the formation of a head to tail binuclear Pt(II) species and as a hydrolytic intermediate in its decomposition, as well.

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**Supporting Information Available:** Tables of atomic positional and displacement parameters, complete bond distances and angles, anisotropic displacement parameters, and hydrogen positional and thermal parameters for **1**, **2**, and **4** (14 pages). Ordering information is given on any current masthead page.

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