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## Synthesis of Platinum Complexes Containing Bridging PTA Ligands

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**Abstract** Two platinum(II) bidentate PTA complexes, *cis,cis*-[PtMe<sub>2</sub>(μ-P,P)<sub>2</sub>(μ-R)<sub>2</sub>PtMe<sub>2</sub>]<sup>4+</sup>4Br<sup>-</sup> [P = PTA, R = C<sub>6</sub>H<sub>4</sub>(*m*-CH<sub>2</sub>-)<sub>2</sub> and C<sub>6</sub>H<sub>3</sub>CH<sub>3</sub>(2,4-CH<sub>2</sub>-)<sub>2</sub>] were synthesized via ligand substitution method by the reactions of 1,1'-[1,3-phenylenebis(methylene)]bis-[3,5-diaza-1-azonia-7-phosphatricyclo(3.3.1.1)]decane dibromide and [1,3-tolylenebis(methylene)]bis-[3,5-diaza-1-azonia-7-phosphatricyclo(3.3.1.1)]decane dibromide with Pt(CH<sub>3</sub>)<sub>2</sub>(η<sup>4</sup>-1,5-cyclooctadiene). These water-soluble bromide salts containing the bridging tertiary phosphine, PTA as well as bridging aryl groups were characterized by NMR spectroscopy, HPLC-MS and elemental analysis. The NMR spectroscopy results suggested that two methyl groups as well as two phosphorus atoms attached to the platinum metal centre were not equivalent to the NMR time scale.

**Keywords** Bidentate PTA, chelated PTA, 1,3,5-triaza-7-phosphaadamantane, binuclear PTA, bis-PTA complex

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### 1. Introduction

The tertiary phosphine, 1,3,5-triaza-7-phosphatricyclo-[3.3.1.1] decane or 1,3,5-triaza-7-phosphaadamantane (PTA or TPA) has considerably high water-solubility (0.235 gm/ml) and air-stability. Also, because of its resistance to oxidation and non-ionic nature, it has drawn a larger attention in recent days [1-2].

Transition metal PTA complexes have their applications in photo-[3], biological [4,5] and medicinal chemistry [6-10]. Because of the lower Tolman cone angle value of the ligand [11], PTA complexes have also widely been reported as catalysts in hydroformylation [12], hydrogenation [13], cross-coupling reactions [14] and many more [15] and some of these reactions have been carried out in aqueous-organic biphasic solvent systems.

Numerous PTA-derivative ligands are known, however, their coordination chemistry is less known [16]. In recent days, we had synthesized a water-soluble PTA-derivative and reported its crystal structure [17], however, its coordination chemistry is still being investigated.

Since the ligand substitution method employing the related η<sup>4</sup>-1,5-cyclooctadiene (COD) is the most efficient way for synthesizing late transition metal PTA and PTA-derivative complexes, a palladium complex containing *N*-coordinated bidentate 7-phospha-3,7-dimethyl-1,3,5-triazabicyclo[3.3.1]nonane (PTN) ligand, [PdCl(CH<sub>3</sub>)(κ<sup>2</sup>-P,N-PTN)], was synthesized by 1:1 reaction of PTN and [PdCl(CH<sub>3</sub>)(COD)] [18]. The resonances corresponding to the methyl protons bonded with the metal and phosphorus with the coupling constant 13.4 Hz and 10.8 Hz, respectively show the ligand's chelated behavior [18]. The water-solubility of bis-PTA ligands, 1,1'-[1,3-phenylenebis(methylene)]bis-[3,5-diaza-1-azonia-7-phosphatricyclo[3.3.1.1]decane dibromide and 1,1'-[1,3-tolylenebis(methylene)]bis-[3,5-diaza-1-azonia-7-phosphatricyclo[3.3.1.1]decane dibromide was found to be more than triple (0.810 gm/ml for both) that of PTA [19]. While the synthesis of these water-soluble xylene-based bis-PTA ligands has been reported [19], their coordination chemistry has not been fully explored yet except an attempt



of preliminary study [20]. On the other hand, while the coordination chemistry as well as catalytic [21] and biological [22] roles of complexes of chelated PTA-derivative ligands has been reported, the catalytic and other applications of the chelated bis-PTA complexes have not yet been reported. Herein, we report the synthesis and characterization of two binuclear Pt(II) coordination complexes containing chelated bis-PTA ligands mentioned above.

## 2. Materials and Methods

### General Comments

Unless otherwise mentioned, the reactions were performed under nitrogen atmosphere on a dual-manifold Schlenk line and dry glassware was used. All the solvents were purchased from Pharmco-Aaper Co. and used after distillation followed by drying over activated 4Å molecular sieves for at least 24 h, unless otherwise stated. CH<sub>3</sub>OH and CH<sub>2</sub>Cl<sub>2</sub> were degassed by freeze-pump-thaw method then stored into the glove box over activated 4Å molecular sieves for at least 24 hours. All other chemicals including 1,3-bis(bromomethyl)benzene, 1,3-bis(bromomethyl)toluene, and PTA were purchased from Sigma Aldrich Chemical Co. NMR spectra were recorded on Bruker Ascend-400 MHz spectrometers at ambient temperature; which was 400 and 161 MHz, for <sup>1</sup>H, and <sup>31</sup>P{<sup>1</sup>H} NMR experiments, respectively. Proton and phosphorus chemical shifts (δ) were reported relative to the residual deuterated solvent and external H<sub>3</sub>PO<sub>4</sub> resonances, respectively. Coupling constants (*J*) were reported in Hertz (Hz) and chemical shifts were reported in parts per million (ppm). Mass spectrometric analysis was carried out on Bruker Esquire 6000 LC-MS spectrometer. 1,1'-[1,3-phenylenebis(methylene)]bis-[3,5-diaza-1-azonia-7-phosphatricyclo(3.3.1.1)]decane dibromide and 1,1'-[1,3-tolylenebis(methylene)]bis-[3,5-diaza-1-azonia-7-phosphatricyclo(3.3.1.1)]decane dibromide were prepared using literature procedure [19].

### Synthesis of *cis,cis*-[PtMe<sub>2</sub>(μ-P,P)<sub>2</sub>(μ-R)<sub>2</sub>PtMe<sub>2</sub>]<sup>4+</sup>4Br<sup>-</sup> [P = PTA, R = C<sub>6</sub>H<sub>4</sub>(*m*-CH<sub>2</sub>)<sub>2</sub>, **1** and C<sub>6</sub>H<sub>3</sub>CH<sub>3</sub>(2,4-CH<sub>2</sub>)<sub>2</sub>, **2**].

A representative reaction for the synthesis of *cis, cis*-[PtMe<sub>2</sub>(μ-P,P)<sub>2</sub>(μ-*m*-phenylene)<sub>2</sub>PtMe<sub>2</sub>]<sup>4+</sup>4Br<sup>-</sup> (**1**) has been described below.

In a 250 ml two-neck round bottom flask containing a magnetic stirrer, 0.114 gm (0.198 mmol) of 1,1'-[1,3-phenylenebis(methylene)]bis-[3,5-diaza-1-azonia-7-phosphatricyclo(3.3.1.1)]decane dibromide and 0.066 gm (0.198 mmol) of Pt(CH<sub>3</sub>)<sub>2</sub>(COD) were placed. The flask was then degassed. 100 ml of degassed methanol and 20 ml of degassed dichloromethane were added through a syringe with continuous stirring. The reaction solution was stirred for 8 hours at room temperature. The reaction mixture was then evaporated to dryness *in vacuo*. The resulting white residue was washed with diethyl ether (2 × 20 ml) and CHCl<sub>3</sub> (2 × 10 ml). The solid was evaporated to dryness *in vacuo*. Complex **1** was obtained as a white solid 71% yield (0.225 gm), based on the dibromide compound. The complex was stored in the glove box. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O): δ 0.44 (br, 6H, Pt-CH<sub>3</sub>), 0.46 (br, 6H, Pt-CH<sub>3</sub>), 4.11 (m, 16H, PCH<sub>2</sub>N), 4.51 (br, 8H, CCH<sub>2</sub>N<sup>+</sup>), 4.65-4.69 (m, 16H, PCH<sub>2</sub>N<sup>+</sup>, NCH<sub>2</sub>N), 5.31 (d, <sup>2</sup>J<sub>HH</sub> = 10.4 Hz, 8H, NCHH'N<sup>+</sup>), 5.40 (d, <sup>2</sup>J<sub>HH</sub> = 10.5 Hz, 8H, NCHH'N<sup>+</sup>), 7.58-7.62 (m, 2H, HPh), 7.70-7.74 (m, 6H, HPh). <sup>31</sup>P{<sup>1</sup>H} NMR (161 MHz, D<sub>2</sub>O): δ -35.8 (d, <sup>1</sup>J<sub>PtP</sub> = 1695 Hz, <sup>2</sup>J<sub>PP</sub> = 9.3 Hz), -37.9 (d, <sup>1</sup>J<sub>PtP</sub> = 1702 Hz, <sup>2</sup>J<sub>PP</sub> = 9.2 Hz). HPLC-MS: *m/z* 1608 [5, (M+H)<sup>+</sup>]. HRMS (ESI) *m/z* calcd for C<sub>44</sub>H<sub>77</sub>N<sub>12</sub>P<sub>4</sub>Br<sub>4</sub>Pt<sub>2</sub> [(M+H)<sup>+</sup>], 1607.8416, found 1607.8419. *Anal. Calcd.* for C<sub>44</sub>H<sub>76</sub>N<sub>12</sub>P<sub>4</sub>Br<sub>4</sub>Pt<sub>2</sub> (1606.8337): C, 32.89; H, 4.77; N, 10.46. *Found:* C, 33.42; H, 4.96; N, 10.70.

### Synthesis of *cis,cis*-[PtMe<sub>2</sub>(μ-P,P)<sub>2</sub>(μ-*m*-tolylene)<sub>2</sub>PtMe<sub>2</sub>]<sup>4+</sup>4Br<sup>-</sup> (**2**).

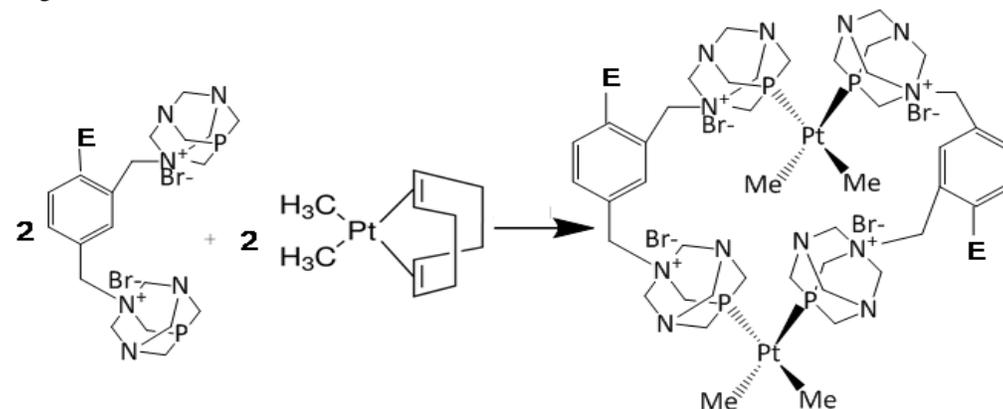
Complex **2** was prepared by following the procedure described for **1**. 0.111 gm (0.197 mmol) of 1,1'-[1,3-tolylenebis(methylene)]bis-[3,5-diaza-1-azonia-7-phosphatricyclo(3.3.1.1)]decane dibromide and 0.066 gm (0.198 mmol) of Pt(CH<sub>3</sub>)<sub>2</sub>(COD). Reaction time: 12 hours. Isolated yield of **2** was 0.181 gm (57%). The complex was stored in the glove box. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O): δ 0.42 (br, 6H, Pt-CH<sub>3</sub>), 0.44 (br, 6H, Pt-CH<sub>3</sub>), 2.58 (s, 6H, CH<sub>3</sub>Ph), 4.06 (m, 16H, PCH<sub>2</sub>N), 4.34 (br, 8H, CCH<sub>2</sub>N<sup>+</sup>), 4.52 (d, <sup>2</sup>J<sub>PH</sub> = 13.2 Hz, 4H, PCHH'N<sup>+</sup>), 4.55 (d, <sup>2</sup>J<sub>PH</sub> = 13.3 Hz, 4H, PCHH'N<sup>+</sup>), 4.64-4.68 (m, 8H, NCH<sub>2</sub>N), 5.23 (d, <sup>2</sup>J<sub>HH</sub> = 10.6 Hz, 8H, NCHH'N<sup>+</sup>), 5.28 (d, <sup>2</sup>J<sub>HH</sub> = 10.7 Hz, 8H, NCHH'N<sup>+</sup>), 7.48-7.61 (m, 6H, HPh). <sup>31</sup>P{<sup>1</sup>H} NMR (161 MHz, D<sub>2</sub>O): δ -35.5 (d, <sup>1</sup>J<sub>PtP</sub> = 1697 Hz, <sup>2</sup>J<sub>PP</sub> = 9.0



Hz),  $-37.7$  (d,  $^1J_{\text{PtP}} = 1705$  Hz,  $^2J_{\text{PP}} = 8.9$  Hz). HPLC-MS:  $m/z$  1622 [7, (M+H)<sup>+</sup>]. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{45}\text{H}_{79}\text{N}_{12}\text{P}_4\text{Br}_4\text{Pt}_2$  [(M+H)<sup>+</sup>], 1621.8682, found 1621.8688. Anal. Calcd. for  $\text{C}_{45}\text{H}_{78}\text{N}_{12}\text{P}_4\text{Br}_4\text{Pt}_2$  (1620.8603): C, 33.35; H, 4.85; N, 10.37. Found: C, 33.86; H, 5.02; N, 10.60.

### 3. Results and Discussion

In an effort to explore the coordination chemistry of bis-PTA ligands of the type P-R-P (P is PTA and R is an aryl group), separate reactions of 1,1'-[1,3-phenylenebis(methylene)]bis-[3,5-diaza-1-azonia-7-phosphatricyclo(3.3.1.1)]decane dibromide and [1,3-tolylenebis(methylene)]bis-[3,5-diaza-1-azonia-7-phosphatricyclo(3.3.1.1)]decane dibromide was carried out with  $\text{Pt}(\text{CH}_3)_2(\text{COD})$  in 1:1 molar ratio (Scheme 1). A tetramethyl Pt(II) bidentate-PTA complex, *cis,cis*-[PtMe<sub>2</sub>( $\mu$ -P,P)<sub>2</sub>( $\mu$ -*m*-phenylene)<sub>2</sub>PtMe<sub>2</sub>]<sup>4+</sup>4Br<sup>-</sup> (**1**) was formed by 1,1'-[1,3-phenylenebis(methylene)]bis-[3,5-diaza-1-azonia-7-phosphatricyclo(3.3.1.1)]decane dibromide in the presence of degassed methanol.



**Scheme 1:** Synthesis of **1** and **2** [E = H, **1** and E = Me (CH<sub>3</sub>), **2**].

Similarly, the reaction of 1,1'-[1,3-tolylenebis(methylene)]bis-[3,5-diaza-1-azonia-7-phosphatricyclo(3.3.1.1)]decane dibromide gave the corresponding tolylene chelated complex **2**. The binuclear complexes, **1** and **2** were obtained as white solids in 71% and 57% yields, respectively. The resulting water-soluble complexes containing the bridging PTA ligands were characterized by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H}NMR spectroscopy, HPLC-MS and elemental analysis.

**Table 1.** <sup>31</sup>P{<sup>1</sup>H}NMR data of **1** and **2**.

Compound	Chemical shift ( $\delta$ ), ppm	<sup>1</sup> J <sub>Pt-P</sub> , Hz	<sup>2</sup> J <sub>P-P</sub> , Hz
<b>1</b>	-35.8, -37.9	1695, 1702	9.3, 9.2
<b>2</b>	-35.5, -37.7	1697, 1705	9.0, 8.9

The <sup>31</sup>P{<sup>1</sup>H}NMR spectra of **1** in D<sub>2</sub>O showed a pair of doublets with <sup>195</sup>Pt satellites, observed at -35.8 and -37.9 ppm with <sup>1</sup>J<sub>Pt-P</sub> coupling constants of 1695 Hz and 1702 Hz, respectively (Table 1). On the other hand, complex **2** showed the spectra of similar pattern at -35.5 and -37.7 ppm with <sup>1</sup>J<sub>Pt-P</sub> coupling constants of 1697 Hz and 1705 Hz, respectively which shows the *cis*-arrangement of methyl groups in these complexes [23,24]. The complexes also displayed <sup>2</sup>J<sub>P-P</sub> coupling in the <sup>31</sup>P NMR spectra. The related chelated salt, *cis,cis*-[PtBr<sub>2</sub>( $\mu$ -P,P)<sub>2</sub>( $\mu$ -R)<sub>2</sub>PtBr<sub>2</sub>]Br<sub>4</sub>, which contained bis-PTA compounds as bridging ligands, exhibited a similar pattern of chemical shifts in the <sup>31</sup>P NMR spectra with <sup>1</sup>J<sub>Pt-P</sub> of 3500 Hz, indicating the *cis*-P,P geometry for the bromo-compound [25]. This leads to conclude that the bis-PTA compounds in **1** and **2** preferentially function as bridging ligands. The LC-MS spectra supported the formation of these complexes, which was further confirmed by the elemental analysis of **1** and **2**. The similar coupling constant values in both **1** and **2** in the <sup>31</sup>P{<sup>1</sup>H} NMR spectra implied that the phenyl backbone R group had little impact on the bidentate (P,P) ligands' basicity. As suggested by the <sup>31</sup>P{<sup>1</sup>H} NMR spectra, the



phosphorus atoms were not found to be equivalent on the NMR time scale. Upon coordination, the bridging structural framework becomes rigid. The  $^1\text{H}$  NMR spectra of the complexes **1** and **2** suggested that two methylene protons belonging to  $\text{NCH}_2\text{N}^+$  as well as  $\text{PCH}_2\text{N}^+$  moieties are not equivalent in the NMR time scale. The same fact is true for two methyl groups bonded to the same metal centre, as indicated by the  $^1\text{H}$  NMR spectroscopy. According to the  $^1\text{H}$  NMR spectroscopy results of the aromatic protons, the complex **2** has the *anti*-conformation with respect to the methyl groups of the aromatic ring [23].

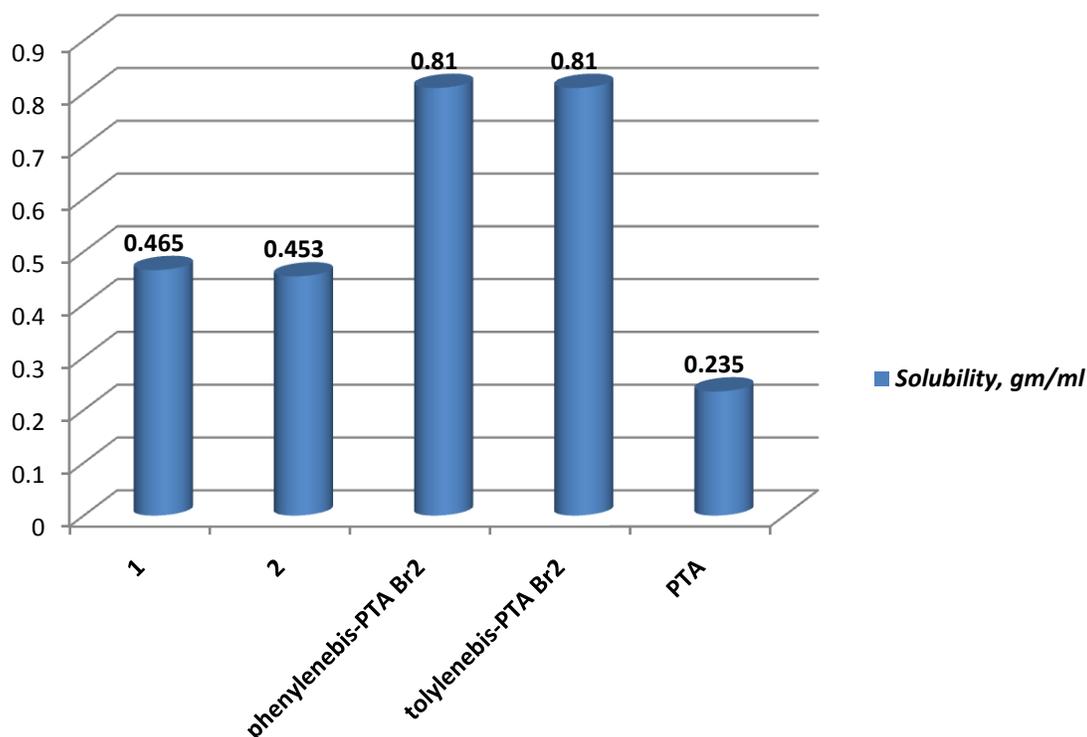


Figure 1: Solubility data of **1** and **2** along with their parent ligands and PTA [19].

The water-solubility of the complexes **1** and **2** was investigated. Based on the preliminary study, the solubility of **1** and **2** in deionized water was found to be 0.465 gm/ml and 0.453 gm/ml, respectively; better than the PTA [19]. The solubility data of **1**, **2**, their parent bis-PTA ligands and PTA has been shown in Figure 1. An attempt to obtain the X-ray diffraction quality single crystal of the complexes **1** and **2** was unsuccessful. While we have added two binuclear platinum complexes to the library of water-soluble complexes containing the chelated bis-PTA ligands, the catalytic and other applications of these complexes are still under investigation.

#### 4. Conclusion

As an addition to the library of water-soluble complexes containing the bridging tertiary phosphine, that is, bidentate version of PTA ligands, we were able to synthesize a pair of Pt-bromide salts bearing such ligands by ligand substitution method. These coordination compounds were characterized by using different spectroscopic techniques. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy results suggested that these complexes had a *cis*-geometry with respect to the methyl groups bonded to the metal centre. The water-solubility of these compounds was investigated. While the multinuclear Pt complexes are known to have higher catalytic activity, the study on catalytic activity of these binuclear platinum complexes is currently underway.

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