

# Synthesis, X-ray Crystal Structure and Luminescence Properties of Binuclear Platinum(II) Complex with PtP<sub>2</sub>S<sub>2</sub> Core and Acetylenic Bridge

Dong-Youn Noh,\* Kyong-Soon Shin, and Kyung-In Son

Department of Chemistry, Seoul Women's University, Seoul 139-774, Korea. \*E-mail: dynoh@swu.ac.kr

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Platinum(II) complexes with ligands of Group 15 and 16 elements such as N, P, O and S have attracted a great deal of attention due to their interesting properties, for example their antitumor activity, electrical conductivity and photophysical properties.<sup>1</sup> Among these complexes, those with a PtP<sub>2</sub>S<sub>2</sub><sup>2-8</sup> or PtN<sub>2</sub>S<sub>2</sub> core<sup>9</sup> were studied as potentially important luminophores. As regards the phosphorous ligand, although it is not used as often as chelating diphosphine ligands such as dppe (1,2-bis(diphenylphosphino)ethylene) and dppf (1,1'-bis(diphenylphosphino)ferrocene),<sup>10</sup> the linear 1,2-bis(diphenylphosphino)acetylene (dppa) was used as a bridging ligand in Cl<sub>2</sub>Pt(μ-dppa)<sub>2</sub>PtCl<sub>2</sub> and its analogues.<sup>11-13</sup> Recently, we reported a facile method of synthesizing a series of binuclear Pt(II) complexes (1,2-dithiolate)Pt(μ-dppa)<sub>2</sub>Pt(1,2-dithiolate), wherein the 1,2-dithiolate ligand contains a methyl sulfide moiety, 1,4-dithiin ring, or carbomethoxy group,<sup>3</sup> as well as their electrochemical properties. Only the complex containing the carbomethoxy group was crystallized, probably because of the lesser constraint of the carbomethoxy group in the 1,2-dithiolate ligand as compared to those containing a methyl sulfide moiety or 1,4-dithiin ring.

In this contribution, we report the results of the X-ray crystal structure analysis and Raman spectroscopic measurement for the (MET)Pt(μ-dppa)<sub>2</sub>Pt(MET) complex (**1**): K<sub>2</sub>(MET) is potassium (Z)-1,4-dimethoxy-1,4-dioxobut-2-ene-2,3-bis(thiolate)) with a carbomethoxy end-group. Also, the luminescence properties of the complex are described in CH<sub>2</sub>Cl<sub>2</sub> at room temperature and 77 K.

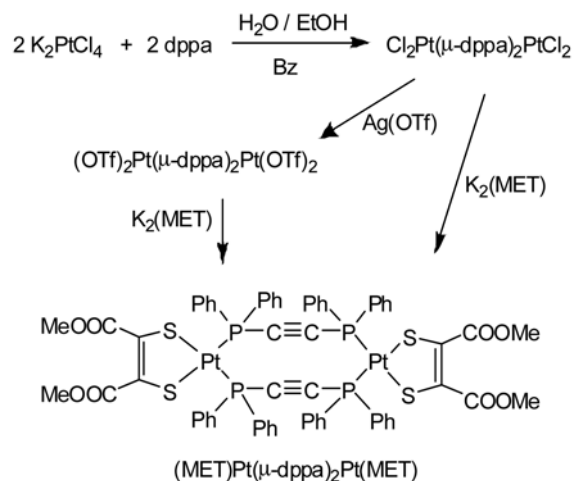
## Experimental

All reactions and recrystallizations were carried out in an environment protected from light and air. The infrared spectra were measured by the KBr pellet method on a MIDAC FT-IR spectrometer. The electronic absorption spectra were obtained in acetonitrile on an HP 8452A diode array spectrometer. The elemental analyses were carried out at the National Center for inter-University Research Facilities (Seoul, Korea). The micro-Raman spectra were recorded at room temperature with a Raman microscope spectrometer (Renishaw Ltd.) equipped with a He:Ne (λ<sub>0</sub> = 632.8 nm) laser, focusing on a 1 μm<sup>2</sup> area. The scattering peaks were calibrated against a Si wafer standard (520 cm<sup>-1</sup>).

**Cl<sub>2</sub>Pt(μ-dppa)<sub>2</sub>PtCl<sub>2</sub>.** This complex was prepared by reacting K<sub>2</sub>PtCl<sub>4</sub> and dppa at a 1:1 molar ratio in a mixed

solvent of EtOH/H<sub>2</sub>O/Benzene, and washed with H<sub>2</sub>O and MeOH (Scheme 1). The FT-IR and <sup>1</sup>H-NMR spectroscopic data of the complex were identical to the previously reported ones.<sup>3</sup> Raman (cm<sup>-1</sup>): 2144 (C≡C), 1648, 1611, 1584 (Ph C=C), 1323, 1182, 1158, 1096, 1025 (Ph C-H), 997 (P-Ph), 699, 614, 578, 325 (Pt-P), 299, 262, 215, 179 (Pt-Cl). UV-vis(CH<sub>3</sub>CN, nm, M<sup>-1</sup>cm<sup>-1</sup>): λ<sub>max</sub> (ε) 274 (19,829), 328 (2,619).

**(MET)Pt(μ-dppa)<sub>2</sub>Pt(MET) (1).** This complex was directly synthesized using Cl<sub>2</sub>Pt(μ-dppa)<sub>2</sub>PtCl<sub>2</sub> and K<sub>2</sub>(MET) as described in ref 3. It was also prepared from Cl<sub>2</sub>Pt(μ-dppa)<sub>2</sub>PtCl<sub>2</sub> via (OTf)<sub>2</sub>Pt(μ-dppa)<sub>2</sub>Pt(OTf)<sub>2</sub> (Scheme 1): An acetonitrile solution of Cl<sub>2</sub>Pt(μ-dppa)<sub>2</sub>PtCl<sub>2</sub> (1 mmol, 0.34 g) and Ag(OTf) (4 mmol, 1.03 g) was stirred for 2 h under an Ar atmosphere. The polycrystalline (OTf)<sub>2</sub>Pt(μ-dppa)<sub>2</sub>Pt(OTf)<sub>2</sub> was separated, washed with acetonitrile and dried *in vacuo*. As the triflate complex was very hygroscopic, it was directly used in the next reaction. A methanol solution of K<sub>2</sub>(MET) (1 mmol, 0.28 g) was added to the CH<sub>3</sub>NO<sub>2</sub> solution of (OTf)<sub>2</sub>Pt(μ-dppa)<sub>2</sub>Pt(OTf)<sub>2</sub> (1 mmol, 1.78 g) and stirred for 2 h under an Ar atmosphere. The precipitated product was filtered, washed with CH<sub>3</sub>NO<sub>2</sub> and dried *in vacuo*. The product was identical to that prepared by the direct method. Yield: 75% (1.19 g). EA: cal. (obs.) C 48.30 (47.82) H 3.29 (3.59). FT-IR (KBr, cm<sup>-1</sup>): 1718, 1703 (C=O), 1238 (C-O). Raman (cm<sup>-1</sup>): 2139 (C≡C), 1704 (C=O), 1651, 1587 (Ph C=C), 1539 (C=C), 1327, 1165, 1102, 1027 (Ph C-H), 1000 (P-Ph), 700, 618, 573, 377 (Pt-P), 267, 210. UV-vis(CH<sub>3</sub>CN,



Scheme 1

**Table 1.** Crystal and structure refinement data for (MET)Pt( $\mu$ -dppa)<sub>2</sub>Pt(MET)

Empirical formula	C <sub>64</sub> H <sub>54</sub> O <sub>9</sub> P <sub>4</sub> Pt <sub>2</sub> S <sub>4</sub>
Formula weight	1609.37
Crystal system	Triclinic
Space group	P $\bar{1}$ (No. 2)
Unit cell dimensions	
<i>a</i> (Å)	14.112(2)
<i>b</i> (Å)	15.530(3)
<i>c</i> (Å)	17.009(3)
$\alpha$ (°)	79.009(15)
$\beta$ (°)	77.535(13)
$\gamma$ (°)	68.590(17)
Volume (Å <sup>3</sup> )	3363.1(10)
<i>Z</i>	2
Calculated density (Mg/m <sup>3</sup> )	1.589
Absorption coefficient (mm <sup>-1</sup> )	4.426
F(000)	1580
Crystal size (mm)	0.35 × 0.35 × 0.25
$\theta$ for data collection (deg.)	1.24 to 25.19
Limiting indices	0 ≤ <i>h</i> ≤ 16, -17 ≤ <i>k</i> ≤ 18, -19 ≤ <i>l</i> ≤ 20
Reflections collected / unique	12608 / 12072 [R(int) = 0.0441]
Data / restraints / parameters	12072 / 0 / 766
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.023
Final R indices [I > 2σ(I)]	R1 = 0.0507, wR2 = 0.1230

**Table 2.** Selected bond distances (Å) and angles (°) for (MET)Pt( $\mu$ -dppa)<sub>2</sub>Pt(MET)

Pt(1)-P(2)	2.263(2)	Pt(1)-P(1)	2.276(3)
Pt(1)-S(1)	2.286(3)	Pt(1)-S(2)	2.290(3)
Pt(2)-P(4)	2.256(3)	Pt(2)-P(3)	2.262(3)
Pt(2)-S(4)	2.286(3)	Pt(2)-S(3)	2.288(3)
C(1)-C(2)	1.341(15)	C(7)-C(8)	1.38(2)
C(13)-C(14)	1.195(13)	C(15)-C(16)	1.195(13)
P(2)-Pt(1)-P(1)	95.94(9)	P(1)-Pt(1)-S(1)	87.35(10)
P(2)-Pt(1)-S(2)	88.33(9)	S(1)-Pt(1)-S(2)	88.54(10)
P(4)-Pt(2)-P(3)	94.32(10)	P(4)-Pt(2)-S(4)	89.40(10)
P(3)-Pt(2)-S(3)	87.93(12)	S(4)-Pt(2)-S(3)	88.72(12)

nm, M<sup>-1</sup>cm<sup>-1</sup>):  $\lambda_{\max}(\epsilon)$  262 (27,900), 344 (5,564).

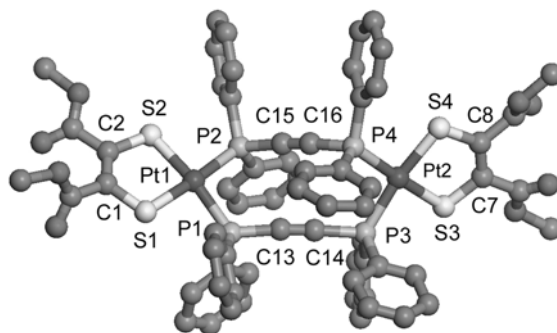
The X-ray diffraction data of complex (**1**) was collected on an Enraf-Nonius CAD4 automatic diffractometer equipped with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) at 293(2) K in the range of 1.24° <  $\theta$  < 25.19°. The structural solution and refinement of the data were handled with the SHELXS-97 and SHELXL-97 programs.<sup>14</sup> The structure was solved by the direct method and refined by the full matrix least-squares method. The crystal and structure refinement data are listed in Table 1, and the selected bond distances and angles are shown in Table 2. The crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC- 611499). These data

can be obtained free of charge via <http://www.ccdc.cam.ac.uk/perl/catreq.cgi>.

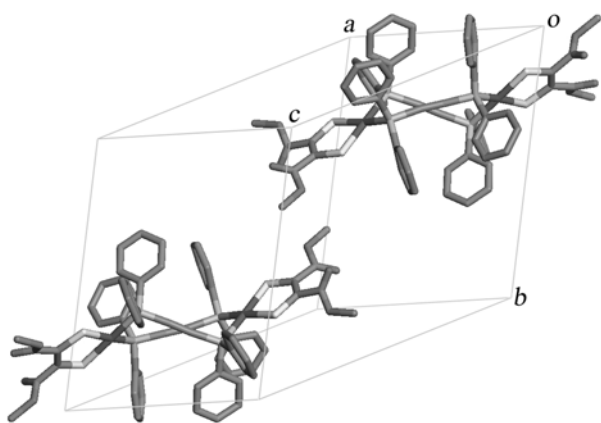
## Results and Discussion

Complex (**1**) was synthesized from Cl<sub>2</sub>Pt( $\mu$ -dppa)<sub>2</sub>PtCl<sub>2</sub> via (OTf)<sub>2</sub>Pt( $\mu$ -dppa)<sub>2</sub>Pt(OTf)<sub>2</sub> in CH<sub>3</sub>NO<sub>2</sub>, as well as by directly reacting Cl<sub>2</sub>Pt( $\mu$ -dppa)<sub>2</sub>PtCl<sub>2</sub> with K<sub>2</sub>(MET) in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH. Even though the indirect method via the triflate complex has to suffer one more step than the direct method, complex (**1**) can easily be isolated by filtration, because it is not soluble in CH<sub>3</sub>NO<sub>2</sub>. On the other hand, since complex (**1**) and Cl<sub>2</sub>Pt( $\mu$ -dppa)<sub>2</sub>PtCl<sub>2</sub> are soluble in CH<sub>2</sub>Cl<sub>2</sub>, more work-up processes are necessary to obtain the pure product in the direct method. The final products prepared by these two methods are identical according to the spectroscopic analyses. Moreover, the Raman spectrum of complex (**1**) shows a peak corresponding to the  $\nu$ (C=O) frequency at 1704 cm<sup>-1</sup> indicating the presence of the MET ligand. The Raman-active stretching vibration of the symmetrical alkyne for complex (**1**) (2139 cm<sup>-1</sup>) is very close to that of Cl<sub>2</sub>Pt( $\mu$ -dppa)<sub>2</sub>PtCl<sub>2</sub> (2144 cm<sup>-1</sup>), which suggests that the ligand exchange of two chlorides for one bidentate dithiolate ligand (MET) does not significantly affect the central alkyne bonds.

The pale-yellow single crystals of complex (**1**) recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH were selected for the X-ray structure analysis. The molecular structure with the selected atomic numbering scheme is shown in Figure 1. It crystallizes in the triclinic system with one molecule of hydrate water. The average bond distances of Pt-S (2.288 Å) and Pt-P (2.264 Å) are comparable to those of analogous complexes with a PtP<sub>2</sub>S<sub>2</sub> core such as mononuclear (MET)Pt(P(OMe)<sub>3</sub>)<sub>2</sub> (2.301 Å and 2.239 Å, respectively)<sup>4</sup> and binuclear (SC<sub>6</sub>F<sub>5</sub>)<sub>2</sub>-Pt( $\mu$ -dppa)<sub>2</sub>Pt(SC<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (2.349 Å and 2.272 Å, respectively).<sup>15</sup> The bond distances of the acetylenic C13≡C14 and C15≡C16 bonds (1.195(13) Å) are fairly well coincident with those of Cl<sub>2</sub>Pt( $\mu$ -dppa)<sub>2</sub>PtCl<sub>2</sub> (1.18-1.19 Å)<sup>3,12</sup> and (SC<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Pt( $\mu$ -dppa)<sub>2</sub>Pt(SC<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (1.19-1.20 Å).<sup>15</sup> The average value of the S-Pt-S bond angle in complex (**1**) is 88.63°, which is 3.8° smaller than that of the (SC<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Pt( $\mu$ -



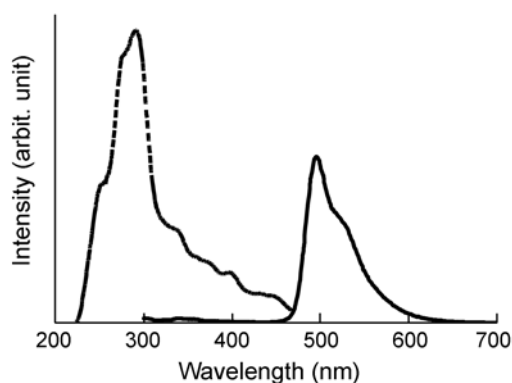
**Figure 1.** Molecular structure of (MET)Pt( $\mu$ -dppa)<sub>2</sub>Pt(MET) complex with the selected atomic numbering scheme. The hydrogen atoms and solvated water molecule are omitted for the sake of clarity.



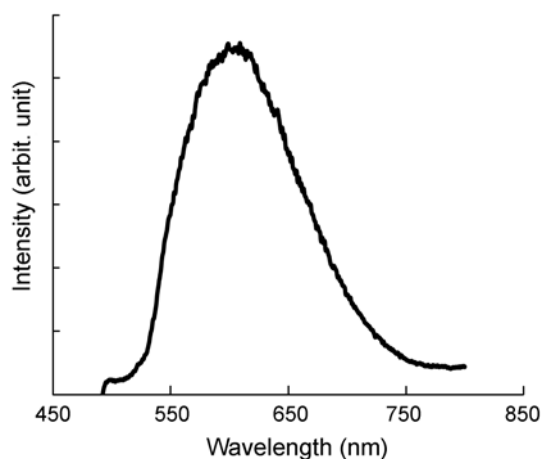
**Figure 2.** Right-handed (lower) and left-handed (upper) isomers of  $(\text{MET})\text{Pt}(\mu\text{-dppa})_2\text{Pt}(\text{MET})$  complex.

$\text{dppa})_2\text{Pt}(\text{SC}_6\text{F}_5)_2$  complex ( $92.43^\circ$ ), due to the presence of the bidentate MET ligand. Also, the square planes around Pt1 ( $\square\text{P2P1S1S2}$ ) and Pt2 ( $\square\text{P3P4S4S3}$ ) are almost planar, with torsion angles of  $6.81^\circ$  and  $8.36^\circ$ , respectively. That is, the two  $\text{PtP}_2\text{S}_2$  cores slightly deviate from a regular square plane, possibly because the carbomethoxy groups on each end of the complex are flexible and disordered, as can be seen in the supplementary crystallographic data. Compared to these  $\text{PtP}_2\text{S}_2$  square planes, the central  $\square\text{P3P1P2P4}$  plane is shown to be more severely distorted with a torsion angle of  $32.04^\circ$ . Due to this distortion, the two acetylenic bonds are staggered relative to each other and, therefore, the whole molecule has a distorted structure (Fig. 2). Another interesting observation concerning the distorted structure of complex (**1**) is that the distortion of the  $\square\text{P3P1P2P4}$  plane is produced in two ways: right-handed and left-handed distortions resulting in two isomers, as shown in Figure 2. The right-handed isomer (lower structure in Fig. 2) is crystallographically related to the left-handed one (upper structure in Fig. 2) by inversion through the coordinate,  $(-x+1, -y+1, -z-1)$ , and complex (**1**) is composed of these two isomers in a 1 : 1 molar ratio.

The absorption spectra of complex (**1**) showed no solvatochromic transition at room temperature in the UV-vis region. Its luminescence properties were investigated at room temperature and 77 K in air-free  $\text{CH}_2\text{Cl}_2$  solution by excitation at 350 nm as shown in Figure 3 and Figure 4, respectively. An emission band with  $\lambda_{\text{max}} = 496$  nm and a shoulder at 522 nm was observed at room temperature, while a broad emission band with  $\lambda_{\text{max}} = 599$  nm was observed at 77 K. These emission bands are much lower in wavelength than those of the mononuclear  $\text{Pt}(\text{P}(\text{OMe})_3)_2$ - $(\text{MET})$  complex (625 and 680 nm at 77 K),<sup>4</sup> which also has the same  $\text{PtP}_2\text{S}_2$  core. The luminescence properties of complex (**1**) with the  $\text{PtP}_2\text{S}_2$  core can be mostly ascribed to the charge-transfer from the  $\text{Pt}(d)/\text{S}(p)$  to  $\text{MET}(\pi^*)$  states, as in the case of the  $\text{Pt}(\text{P}(\text{OMe})_3)_2$ - $(\text{MET})$  complex,<sup>4</sup> possibly due to the influence of structural factors such as the planarity of the  $\text{PtP}_2\text{S}_2$  square, the distortion of the  $\square\text{P3P1P2P4}$  plane and the flexibility of the carbomethoxy groups. The lifetime



**Figure 3.** Room temperature emission (solid line;  $\lambda_{\text{max}} = 496$  nm) and excitation (dashed line;  $\lambda_{\text{ex}} = 350$  nm) spectra of  $(\text{MET})\text{Pt}(\mu\text{-dppa})_2\text{Pt}(\text{MET})$  complex in  $\text{CH}_2\text{Cl}_2$ .



**Figure 4.** Low temperature (77 K) emission spectra of  $(\text{MET})\text{Pt}(\mu\text{-dppa})_2\text{Pt}(\text{MET})$  complex in  $\text{CH}_2\text{Cl}_2$  ( $\lambda_{\text{max}} = 599$  nm).

of the luminescence of complex (**1**) at 77 K was estimated to be 78 ns by fitting its decay curve. This value is two orders of magnitude shorter than that of the  $(\text{dppe})\text{PtS}_2$  ( $\text{S}_2$ : 1,2-dithiolate substituted with pyridinium<sup>7</sup> or quinoxaline<sup>8</sup>), but two orders of magnitude longer than that of the  $(\text{dppe})\text{PtS}_2$  ( $\text{S}_2$ : pyridyl-substituted 1,2-dithiolate),<sup>6</sup> all of which have the same  $\text{PtP}_2\text{S}_2$  core.

In summary, a binuclear Pt(II) complex with acetylenic bridges  $(\text{MET})\text{Pt}(\mu\text{-dppa})_2\text{Pt}(\text{MET})$  (**1**) was synthesized from  $\text{Cl}_2\text{Pt}(\mu\text{-dppa})_2\text{PtCl}_2$  via  $(\text{OTf})_2\text{Pt}(\mu\text{-dppa})_2\text{Pt}(\text{OTf})_2$ , and found to crystallize in a triclinic system. The  $\text{PtP}_2\text{S}_2$  squares are almost planar, but the central  $\square\text{P3P1P2P4}$  plane is severely distorted (a torsion angle of  $32.04^\circ$ ) resulting in two isomers (right- and left-handed ones) being paired in the crystal structure. The carbomethoxy end groups are flexible and quite disordered. In order to investigate its luminescence properties, complex (**1**) dissolved in  $\text{CH}_2\text{Cl}_2$  solution was excited at 350 nm. The emission band was observed at  $\lambda_{\text{max}} = 496$  nm (298 K) and at  $\lambda_{\text{max}} = 599$  nm (77 K). The lifetime of the luminescence at 77 K was estimated to be 78 ns.

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