

Synthesis, X-ray Crystal Structure and Luminescence Properties of Binuclear Platinum(II) Complex with PtP₂S₂ Core and Acetylenic Bridge

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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.¹ Among these complexes, those with a PtP₂S₂²⁻⁸ or PtN₂S₂ core⁹ 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 dpfp (1,1'-bis(diphenylphosphino)ferrocene),¹⁰ the linear 1,2-bis(diphenylphosphino)acetylene (dppa) was used as a bridging ligand in Cl₂Pt(μ-dppa)₂PtCl₂ and its analogues.¹¹⁻¹³ Recently, we reported a facile method of synthesizing a series of binuclear Pt(II) complexes (1,2-dithiolate)Pt(μ-dppa)₂Pt(1,2-dithiolate), wherein the 1,2-dithiolate ligand contains a methyl sulfide moiety, 1,4-dithiin ring, or carbomethoxy group,³ 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)₂Pt(MET) complex (**1**: K₂(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 CH₂Cl₂ at room temperature and 77 K.

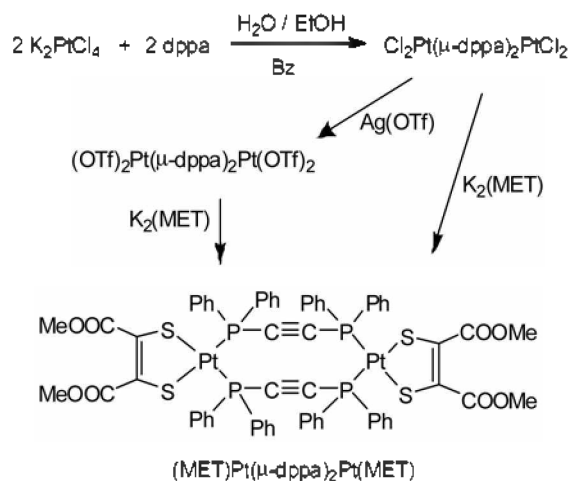
Experimental

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_o = 632.8 nm) laser, focusing on a 1 μm² area. The scattering peaks were calibrated against a Si wafer standard (520 cm⁻¹).

Cl₂Pt(μ-dppa)₂PtCl₂. This complex was prepared by reacting K₂PtCl₄ and dppa at a 1:1 molar ratio in a mixed

solvent of EtOH/H₂O/Benzene, and washed with H₂O and MeOH (Scheme 1). The FT-IR and ¹H-NMR spectroscopic data of the complex were identical to the previously reported ones.³ Raman (cm⁻¹): 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(CH₃CN, nm, M⁻¹cm⁻¹): λ_{max} (ε) 274 (19,829), 328 (2,619).

(MET)Pt(μ-dppa)₂Pt(MET) (1). This complex was directly synthesized using Cl₂Pt(μ-dppa)₂PtCl₂ and K₂(MET) as described in ref 3. It was also prepared from Cl₂Pt(μ-dppa)₂PtCl₂ via (OTf)₂Pt(μ-dppa)₂Pt(OTf)₂ (Scheme 1): An acetonitrile solution of Cl₂Pt(μ-dppa)₂PtCl₂ (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)₂Pt(μ-dppa)₂Pt(OTf)₂ 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 K₂(MET) (1 mmol, 0.28 g) was added to the CH₃NO₂ solution of (OTf)₂Pt(μ-dppa)₂Pt(OTf)₂ (1 mmol, 1.78 g) and stirred for 2 h under an Ar atmosphere. The precipitated product was filtered, washed with CH₃NO₂ 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⁻¹): 1718, 1703 (C=O), 1238 (C-O), Raman (cm⁻¹): 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(CH₃CN,



Scheme 1

Table 1. Crystal and structure refinement data for (MET)Pt(μ -dppa)₂Pt(MET)

| | |
|--|--|
| Empirical formula | C ₆₄ H ₅₄ O ₉ P ₄ Pt ₂ S ₄ |
| 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) |
| α (°) | 79.009(15) |
| β (°) | 77.535(13) |
| γ (°) | 68.590(17) |
| Volume (Å ³) | 3363.1(10) |
| <i>Z</i> | 2 |
| Calculated density (Mg/m ³) | 1.589 |
| Absorption coefficient (mm ⁻¹) | 4.426 |
| F(000) | 1580 |
| Crystal size (mm) | 0.35 × 0.35 × 0.25 |
| θ 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> ² | 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(μ -dppa)₂Pt(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⁻¹cm⁻¹): $\lambda_{\max}(\epsilon)$ 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 α radiation ($\lambda = 0.71073$ Å) at 293(2) K in the range of 1.24° < θ < 25.19°. The structural solution and refinement of the data were handled with the SHELXS-97 and SHELXL-97 programs.¹⁴ 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 Cl₂Pt(μ -dppa)₂PtCl₂ via (OTf)₂Pt(μ -dppa)₂Pt(OTf)₂ in CH₃NO₂, as well as by directly reacting Cl₂Pt(μ -dppa)₂PtCl₂ with K₂(MET) in CH₂Cl₂/CH₃OH. 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 CH₃NO₂. On the other hand, since complex (1) and Cl₂Pt(μ -dppa)₂PtCl₂ are soluble in CH₂Cl₂, 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 ν (C=O) frequency at 1704 cm⁻¹ indicating the presence of the MET ligand. The Raman-active stretching vibration of the symmetrical alkyne for complex (1) (2139 cm⁻¹) is very close to that of Cl₂Pt(μ -dppa)₂PtCl₂ (2144 cm⁻¹), 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 CH₂Cl₂/CH₃OH 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 PtP₂S₂ core such as mononuclear (MET)Pt(P(OMe)₃)₂ (2.301 Å and 2.239 Å, respectively)⁴ and binuclear (SC₆F₅)₂Pt(μ -dppa)₂Pt(SC₆F₅)₂ (2.349 Å and 2.272 Å, respectively).¹⁵ The bond distances of the acetylenic C13=C14 and C15=C16 bonds (1.195(13) Å) are fairly well coincident with those of Cl₂Pt(μ -dppa)₂PtCl₂ (1.18-1.19 Å)^{3,12} and (SC₆F₅)₂Pt(μ -dppa)₂Pt(SC₆F₅)₂ (1.19-1.20 Å).¹⁵ 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 (SC₆F₅)₂Pt(μ -

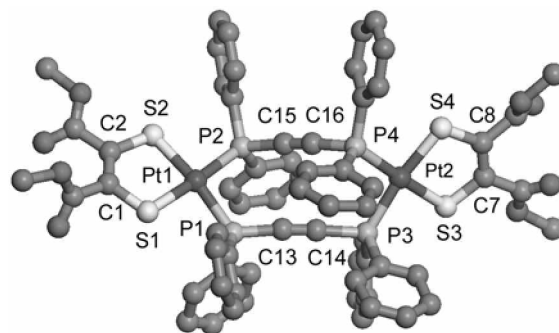


Figure 1. Molecular structure of (MET)Pt(μ -dppa)₂Pt(MET) complex with the selected atomic numbering scheme. The hydrogen atoms and solvated water molecule are omitted for the sake of clarity.

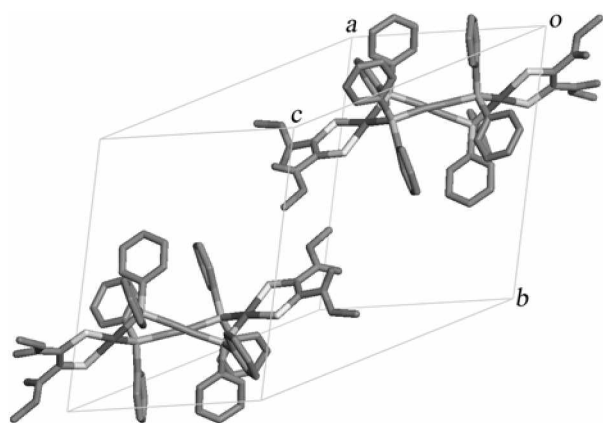


Figure 2. Right-handed (lower) and left-handed (upper) isomers of $(\text{MET})\text{Pt}(\mu\text{-dppa})_2\text{Pt}(\text{MET})$ complex.

$\text{dppa})_2\text{Pt}(\text{SC}_6\text{F}_5)_2$ complex (92.43°), 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° and 8.36° , respectively. That is, the two PtP_2S_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 PtP_2S_2 square planes, the central $\square\text{P3P1P2P4}$ plane is shown to be more severely distorted with a torsion angle of 32.04° . 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 CH_2Cl_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 $\text{Pt}(\text{P}(\text{OME})_3)_2\text{-}(\text{MET})$ complex (625 and 680 nm at 77 K),⁴ which also has the same PtP_2S_2 core. The luminescence properties of complex (1) with the PtP_2S_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 $\text{Pt}(\text{P}(\text{OME})_3)_2\text{-}(\text{MET})$ complex,⁴ possibly due to the influence of structural factors such as the planarity of the PtP_2S_2 square, the distortion of the $\square\text{P3P1P2P4}$ plane and the flexibility of the carbomethoxy groups. The lifetime

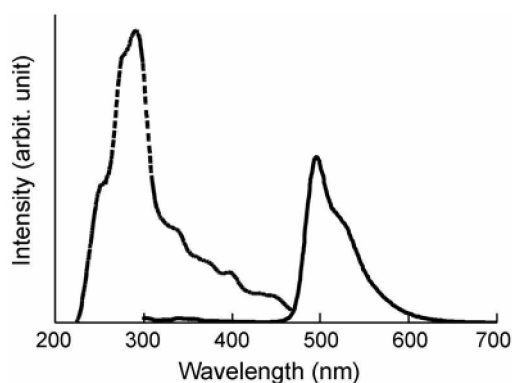


Figure 3. Room temperature emission (solid line; $\lambda_{\text{max}} = 496$ nm) and excitation (dashed line; $\lambda_{\text{ex}} = 350$ nm) spectra of $(\text{MET})\text{Pt}(\mu\text{-dppa})_2\text{Pt}(\text{MET})$ complex in CH_2Cl_2 .

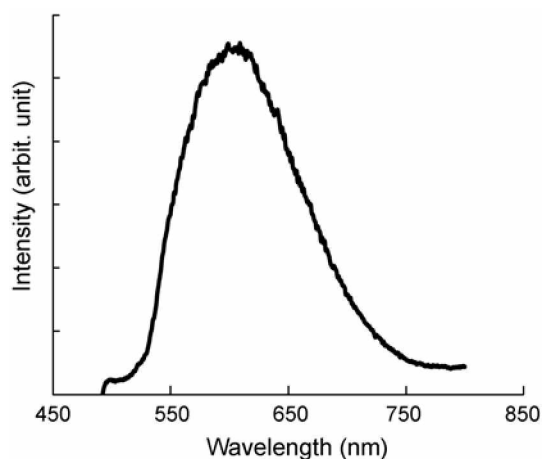


Figure 4. Low temperature (77 K) emission spectra of $(\text{MET})\text{Pt}(\mu\text{-dppa})_2\text{Pt}(\text{MET})$ complex in CH_2Cl_2 ($\lambda_{\text{max}} = 599$ nm).

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 $(\text{dpppe})\text{PtS}_2$ (S_2 : 1,2-dithiolate substituted with pyridinium⁷ or quinoxaline⁸), but two orders of magnitude longer than that of the $(\text{dpppe})\text{PtS}_2$ (S_2 : pyridyl-substituted 1,2-dithiolate),⁶ all of which have the same PtP_2S_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 PtP_2S_2 squares are almost planar, but the central $\square\text{P3P1P2P4}$ plane is severely distorted (a torsion angle of 32.04°) 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 CH_2Cl_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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