Binuclear Platinum(II) Building-blocks for the Metal-coordinated Self-assembly: (Dithiolate)Pt(μ-dppa)$_2$Pt(dithiolate) where dppa = Bis(diphenylphosphino)acetylene

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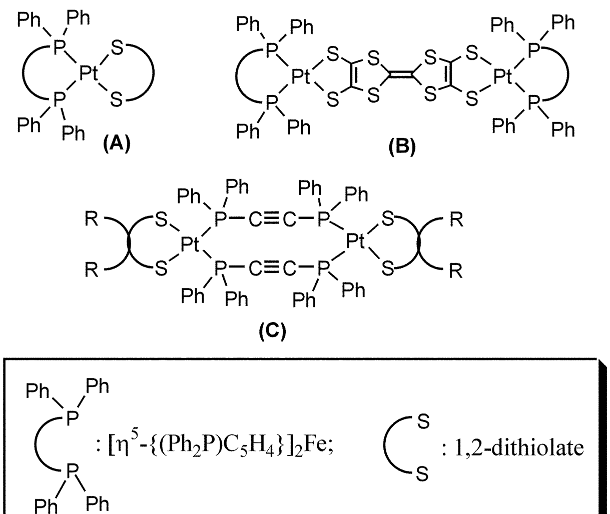
Received September 19, 2003

Key Words : Pt(II) dithiolate, Dppa, Cyclic voltammetry, Building-block, ^{31}P-/^{195}Pt-NMR

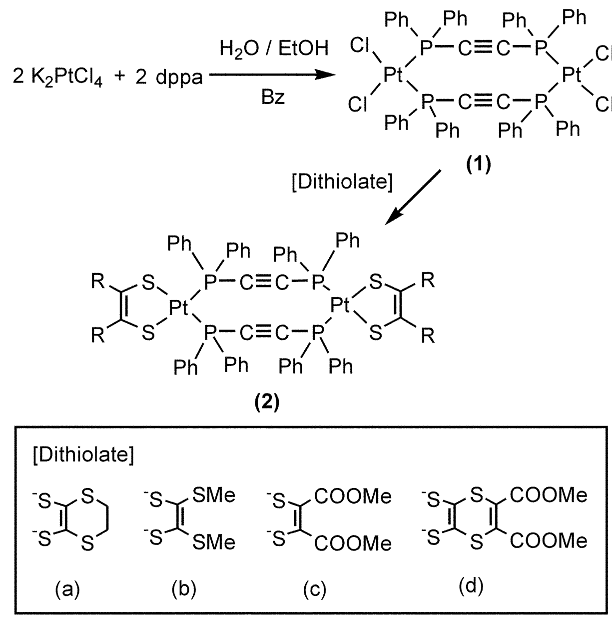
One of the most important research topics in coordination polymer chemistry in recent times has been the development of new building blocks,[1-5] able to construct new types of self-assembly exhibiting unique structural, chemical and physical properties. The coordinating ligand of interest is dppa (bis(diphenylphosphino)acetylene), which has a linear geometry with two terminal phosphine moieties and one acetylene moiety able to coordinate to metal ions. One of the potential building blocks using dppa would appear to be $Cl_2Pt(\mu\text{-dppa})_2PtCl_2$ (**1**), in which two Pt(II) ions are bridged by two dppa ligands and terminated by two chloride ions.[2,3] Even though its utility as a building block in new types of self-assembly has not been previously reported, $Cl_2Pt(\mu\text{-dppa})_2PtCl_2$ (**1**), together with its Pd(II) and Pd(II)/Pt(II) analogues, seems to be highly suitable for such purposes.[2-4]



Recently, we reported on a series of mono- and bi-nuclear complexes, having a P_2PtS_2 core (**A** and **B**), and wherein the 1,2-dithiolate ligands contain cyanide, methyl sulfide, 1,4-dithiin ring, and tetrathiafulvalene (TTF) derivatives.[5] In this paper, we report on a facile synthetic route with a very high yield and the less strained molecular structure of $Cl_2Pt(\mu\text{-dppa})_2PtCl_2$ (**1**). Moreover, the extension of this bi-nuclear complex by substituting chloride ions with the functionalized 1,2-dithiolate ligands is achieved and the resultant complexes are characterized by high-resolution MALDI-MS, ^{31}P-/^{195}Pt-NMR and cyclic voltammetry.

Experimental Section

Dithiolate ligands (**a-d**) were prepared according to the literature procedures.[5,6] All reactions and recrystallizations involving platinum complexes were carried out under conditions of protection from light and air. Elemental analysis was carried out at the National Center for inter-University Research Facilities in Seoul. The FAB mass spectrum of **1** was taken with a JMS-HX110/110A tandem mass spectrometer (JEOL), and the MALDI mass spectra of **2** were taken with a Voyager-DE STR mass spectrometer (Applied Biosystems). ^{31}P and ^{195}Pt NMR spectra were measured at the Advanced Analysis Center at KIST. Infrared spectra were obtained by the KBr pellet method on a MIDAC FT-IR spectrometer, and the UV-vis spectra were obtained in acetonitrile on a HP 8452A diode array spectrometer. Cyclic voltammetry measurements were carried out at room temperature with a CHI620A Electrochemical Analyzer (CHI Instruments Inc.) in 10 mL CH_2Cl_2 solution containing a 0.01 mM sample, using 0.1 M $n\text{-}Bu_4N{\cdot}BF_4$ as



Scheme 1. Synthesis of complexes **1** and **2**.

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the electrolyte, Ag/Ag^+ as the reference electrode, a Pt-button working electrode (r = 1 mm), a platinum wire as the counter electrode and with a 0.04 V s^{-1} scan rate ($E_{1/2}$ = 0.694 V for Fc/Fc^+ couple).

Bis[μ-{(diphenylphosphino)acetylene}] bis(dichloroplatinum). To an ethanol suspension (24 mL) of K_2PtCl_4 (0.84 g, 2 mmol) was added a minimum amount of degassed water prepared by argon bubbling with heating prior to use, until the suspension became clear. A benzene solution (10 mL) of dppa (0.79 g, 2 mmol) was dropped into this solution, which led to the immediate formation of a white precipitate. For the completion of the reaction, the reaction mixture was stirred for 6 hrs. The white precipitate was filtered and washed with distilled water and methanol, and recrystallized from CH_2Cl_2/MeOH. Yield: 93% (1.23 g). M.p 207-208 °C (dec.). EA: calc for $C_{52}H_{40}Cl_4P_4Pt_2$ C 47.29, H 3.05; obsd C 47.30, H 3.05. FAB-MS (*m/z*): 1320.38 (M^++2). ^{31}P NMR ($CDCl_3$): δ -13.76. ^{195}Pt NMR ($CDCl_3$): δ -4431 (t, ^1J (Pt, P) = 3660 Hz). FT-IR (KBr, cm^{-1}): 3054 (Ph C-H str), 1480, 1437 (Ar ip str), 1185, 1161, 1099 (ip CH def), 1026, 998 (P-Ph str), 837, 744 (oop CH def), 689, 545, 515, 494, 442 (oop ring def).

Bis[μ-{(diphenylphosphino)acetylene}] bis(platinum-dithiolate). To an ethanol suspension (10 mL) of the 1,3-dithiol-2-on precursors of the corresponding dithiolate (2 mmol; 0.44 g (**a**), 0.42 g (**b**), 0.48 g (**c**), 0.65 g (**d**)) was added potassium hydroxide (0.21 g, 4 mmol) with stirring for 30 min under an argon atmosphere. $(PtCl_2)_2(\mu\text{-dppa})_2$ (1 mmol, 1.34 g) dissolved in a minimum amount of methylene chloride (40 mL) was added, followed by stirring at room temperature for 4 h. The precipitate was filtered off and washed with methylene chloride, a small amount of dilute acid and H_2O. The filtrate was dried under reduced pressure and then recrystallized from CH_2Cl_2/MeOH.

For **2a**: Yield: 65% (0.99 g). M.p 179-180 °C (dec.). MALDI-MS (*m/z*): 1539 (M^++1), 1511 (M^++1-CH_2CH_2), 1355 (M^++1-2SCH_2CH_2S). ^{31}P NMR ($CDCl_3$): δ -8.036. ^{195}Pt NMR ($CDCl_3$): δ -4742 (t, ^1J (Pt, P) = 2864 Hz). FT-IR (KBr, cm^{-1}): 3053 (Ph C-H str), 2919, 2854 (-CH_2-CH_2-), 2057 (-C≡C-), 1626 (-C=C-), 1480, 1436 (Ar ip str), 1161, 1098 (ip CH def), 1026, 999 (P-Ph str), 836, 744 (oop CH def), 691, 537, 514, 497 (oop ring def). UV (CH_3CN, nm): 208s, 228sh, 254sh.

For **2b**: Yield: 60% (0.93 g). M.p 167-168 °C (dec.). MALDI-MS (*m/z*): 1539 (M^+-3), 1512 (M^+-2CH_3), 1354 (M^++1-4SCH_3). ^{31}P NMR ($CDCl_3$): δ -8.064. ^{195}Pt NMR ($CDCl_3$): δ -4742 (t, ^1J (Pt, P) = 2865 Hz). FT-IR (KBr, cm^{-1}): 3051 (Ph C-H str), 2917, (-CH_3), 2054 (-C≡C-), 1654 (-C=C-), 1480, 1436 (Ar ip str), 1185, 1131, 1098 (ip CH def), 1026, 998 (P-Ph str), 834, 744 (oop CH def), 691, 537, 514, 497, 436 (oop ring def). UV (CH_3CN, nm): 212s, 226sh, 254sh.

For **2c**: Yield: 72% (1.15 g). M.p 132-133 °C (dec.). MALDI-MS (*m/z*): 1590 (M^+), 1560 (M^+-2CH_3). ^{31}P NMR ($CDCl_3$): δ -8.377. ^{195}Pt NMR ($CDCl_3$): δ -4663 (t, ^1J (Pt, P) = 2818 Hz). FT-IR (KBr, cm^{-1}): 3056 (Ph C-H str), 2980, 2945 (-CH_3), 2054 (-C≡C-), 1718, 1703 (COO) 1629 (-C=C-), 1480, 1437 (Ar ip str), 1238 (COO), 1097 (ip CH def), 1030, 999 (P-Ph str), 838, 745 (oop CH def), 691, 538, 514, 497, 436 (oop ring def). UV (CH_3CN, nm): 208s, 230sh, 254sh, 346w.

For **2d**: Yield: 63% (1.11 g). M.p 163-164 °C (dec.). MALDI-MS (*m/z*): 1767 (M^++1). ^{31}P NMR ($CDCl_3$): δ -8.753. ^{195}Pt NMR ($CDCl_3$): δ -4506 (t, ^1J (Pt, P) = 2825 Hz). FT-IR (KBr, cm^{-1}): 3054 (Ph C-H str), 2948 (-CH_3), 2054 (-C≡C-), 1722 (COO) 1626 (-C=C-), 1480, 1436 (Ar ip str), 1245 (COO), 1097 (ip CH def), 1021 (P-Ph str), 836, 745 (oop CH def), 691, 537, 514, 497, 453 (oop ring def). UV (CH_3CN, nm): 212s 226sh.

X-ray crystal structure analysis. A white single crystal with dimensions of 0.40 × 0.28 × 0.25 mm was selected for the x-ray diffraction experiment and the reflection data were collected on an Enraf-Nonius CAD4 automatic diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71071 Å) at 293(2) K. The structure solution and refinement of the data were handled with the SHELXS-97 and SHELXL-97 programs.[7] Crystal data for $C_{52}H_{40}Cl_4P_4Pt_2$ $(CH_2Cl_2)_2$; Orthorhombic, Pbcn, a = 14.201(3) Å, b = 17.643(4) Å, c = 21.836(8) Å, V = 5471(2) Å^3, Z = 4, Dc = 1.810 mg/m^3; 5108 reflections collected, 3449 independent reflections, final R_1 = 0.0336, wR_2 = 0.0800. Crystallographic data for $(PtCl_2)_2(\mu\text{-dppa})_2\cdot(CH_2Cl_2)_2$ have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-216410). The data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/perl/catreq/catreq.cgi (or from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

Complex **1** was synthesized using equimolar amounts of K_2PtCl_4 and dppa in a mixed-solvent (ethanol/water/benzene) without exposure to air and light (Scheme 1).[5] This can be regarded as a facile synthetic route to complex **1**, because the reaction is carried out at room temperature, simply by stirring the reaction mixture, and it gives a very high yield (93%) after recrystallization. Moreover, the same product can be obtained even when the reactant ratio (K_2PtCl_4 over dppa) varies from 0.5 to 2.0. Four kinds of 1,2-dithiolate ligands (**a-d**) were treated with complex **1** to yield complexes **2** (60-72%), which in each case were washed with a small amount of dilute acid to eliminate any possibility of the potassium ion coordinated to the acetylenic triple bond. Since the stretching vibration of a symmetrical alkyne is infrared inactive,[8] no ν(C≡C) vibrations were observed in the IR spectra of either dppa or complex **1**. Complex **2** has the same dithiolate ligand at each end and therefore seems to have a symmetrical structure. However, all of these complexes show a small IR band at around 2054 cm^{-1}, which is attributed to an ν(C≡C) vibration. From these observations, it is believed that the various functional groups, such as ethylene, methyl sulfide and methyl ester, attached to the dithiolate ligand, must be disordered and, therefore, complex **2** is totally unsymmetrical in the solid state.

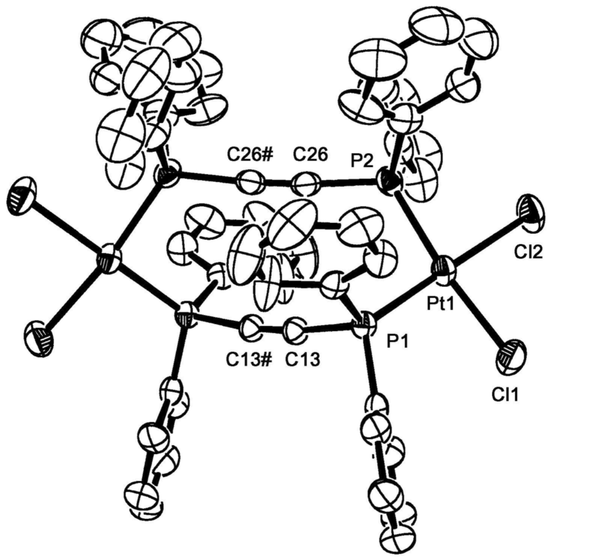

Figure 1. ORTEP drawing of $Cl_2Pt(\mu\text{-dppa})_2PtCl_2$ with the atomic numbering scheme. Hydrogen atoms and solvated CH_2Cl_2 molecules are omitted for clarity. Selected bond distances (Å) and angles (°): Pt1-Cl1 2.322(2), Pt1-Cl2 2.343(2), Pt1-P1 2.2382(19), Pt1-P2 2.239(2), C13-C13# 1.175(13), C26-C26# 1.182(14), P1-Pt1-P2 96.04(7), P1-Pt1-Cl1 91.46(7), P2-Pt1-Cl2 85.53(8), Cl1-Pt1-Cl2 87.06(8), C13#-C13-P1 173.2(3), C26#-C26-P2 171.3(9) (#: -x+1, y, -z+3/2).

A single crystal of complex **1** suitable for X-ray structure analysis was obtained by the diffusion process involving CH_2Cl_2 and MeOH. The molecular structure along with the selected atomic numbering scheme is shown in Figure 1. The P_2PtCl_2 core has a distorted square planar geometry with angles of 96.04(7)° for P1-Pt1-P2 and 87.06(8)° for Cl1-Pt1-Cl2. The C13=C13# and C26=C26# bond distances are 1.175(13) Å and 1.182(14) Å, respectively, which are comparable to those in $PtPdCl_4(dppa)_2$ (1.195(9) Å),[4] $Pd_2Cl_4(dppa)_2$ (1.199(4) Å)[3] and $Pt_2Cl_4(dppa)_2$ (1.16(2) Å and 1.22(2) Å)[3]. The angles P1-C13-C13# (173.2(3)°) and P2-C26-C26# (171.3(9)°) of complex **1** deviate from those of the linear conformation. These observations indicate that this complex has a distorted conformation especially around the Pt ion, but the distortion is not as big as was previously reported.[3] This distorted conformation probably influences the formation of complex **2**: The 1,2-dithiolate ligands with the six-membered 1,4-dithiin ring (**a** and **d**) or the open structure (**b** and **c**) successfully react with complex **1** to produce the well-characterized complex **2**. From our preliminary synthetic result, however, we were not able to produce complex **2** with the 1,3-dithiol-2-thione-4,5-dithiolate (dmit) ligand, which contains the more constrained five-membered 1,3-dithiol-2-thione ring. It is likely that the possible tension around the Pt ion prohibits the formation of complex **2** with the dmit ligand.

Table 1. Cyclic voltammetry parameters for the complexes (in Volts)*

Complex	E_{pa}^1	E_{pc}^1	ΔE_p^1	$E_{1/2}^1$	E_{pa}^2
1	1.344	1.028	–	–	–
2a	0.854	0.718	0.136	0.786	1.420
2b	0.858	0.712	0.146	0.785	1.420
2c	0.884	0.606	0.278	0.745	1.442
2d	1.072	0.948	0.124	1.010	1.506

*0.04 V s^{-1} scan rate, 0.01 mM samples in CH_2Cl_2 at 298 K, Pt disk electrode (3.14 mm^2), supporting electrolyte: *n*-$Bu_4N\cdot BF_4$ 0.1 M, reference electrode: Ag/Ag^+.

Cyclic voltammograms (CV) of complexes **1** and **2** were measured between 0 V and 1.6 V using a Pt disk electrode, and the electrochemical parameters for these complexes are summarized in Table 1. Complex **1** exhibits one irreversible redox peak at $E_{pa} = 1.344$ V and $E_{pc} = 1.028$ V. The complexes **2** show almost identical CV patterns with one reversible peak ($E_{1/2}^1$), attributable to the redox process of the dithiolate ligands, and one oxidation peak (E_{pa}^2), attributable to that of the $(dppa)_2Pt_2$ moiety. Complexes **2a** and **2b** exhibit almost the same $E_{1/2}^1$ and E_{pa}^2 values, suggesting that the presence of the 1,4-dithiin ring in ligand **a** does not cause the redox potential to differ significantly from that of ligand **b**. On the other hand, ligands **c** and **d**, which have two methyl ester terminal groups, have different redox potentials. The redox potential of complex **2c** is close to those of complexes **2a** and **2b**, possibly because ligand **c** has an open structure similar to that of ligand **b**. In the case of complex **2d**, however, ligand **d** has an additional 1,4-dithiin ring, which may increase the $E_{1/2}^1$ and E_{pa}^2 values, due to electron delocalization over the ligand **d**. The ligands **b**, **c** and **d** all have potential secondary coordinating groups, such as sulfide and ester moieties. These terminal groups can accommodate some transition metal ions, so that the corresponding complex **2** can be used as a new building block for the construction of the self-assembly.

Acknowledgement. This work was supported by Seoul Womens University (2003 Special Research Grant).

References

1. (a) Fujita, M. In *Molecular Self-assembly Organic versus Inorganic Approaches*; Fujita, M., Ed.; Springer: Berlin, 2000. (b) Sun, S. S.; Anspach, J. A.; Lees, A. J.; Zavalij, P. Y. *Organometallics* **2002**, *21*, 685.
2. Carty, A. J.; Efraty, A. *Inorg. Nucl. Chem. Letters* **1968**, *4*, 427.
3. Oberhauser, W.; Bachmann, C.; Stampfl, T.; Bruggeller, P. *Inorg. Chim. Acta* **1997**, *256*, 223.
4. Clark, H.; Ferguson, G.; Kapoor, P. N.; Parvez, M. *Inorg. Chem.* **1985**, *24*, 3924.
5. (a) Noh, D. Y.; Seo, E. M.; Lee, H. J.; Jang, H. Y.; Choi, M. G.; Kim, H. Y.; Hong, J. *Polyhedron* **2001**, *20*, 1939. (b) Shin, K. S.; Han, Y. K.; Noh, D. Y. *Bull. Korean Chem. Soc.* **2003**, *24*, 235.
6. (a) Varma, K. S.; Bury, A.; Harris, N. J.; Underhill, A. E. *Synthesis* **1987**, 837. (b) Svenstrup, N.; Becker, J. *Synthesis* **1995**, 215.
7. Sheldrick, G. M. *SHELXS-97 and SHELXL-97: A Program for Structure Determination and Refinement*; University of Göttingen: Germany, 1997.
8. Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectroscopic Identification of Organic Compounds*; Wiley: Singapore, 1991; pp 107-108.