CHEMISTRY LETTERS, pp. 2061-2064, 1993.

Novel Metal Substitution Reactions in Amidate-Bridged Binuclear Complexes $[M_2(bpy)_2(3,3\text{-DMGI})_2]^{2+}$ (M = Pt(II), Pd(II); bpy = 2,2'-bipyridine; 3,3-DMGI = 3,3-dimethylglutarimidate)

Kazuko MATSUMOTO* and Hiroshi URATA

Department of Chemistry, Waseda University, Shinjuku-ku, Tokyo 169

The reaction of $[Pt_2(bpy)_2(3,3\text{-DMGI})_2]^{2+}$ with Pd(bpy)Cl_2 produces $[PtPd(bpy)_2(3,3\text{-DMGI})_2]^{2+}$. The same compound is obtained also from the reaction of $[Pd_2(bpy)_2(3,3\text{-DMGI})_2]^{2+}$ with Pt(bpy)Cl_2. The crystal structures of these complexes are reported.

Many amidate-bridged $Pt(II)_2$ and $Pd(II)_2$ dimer complexes of a general formula $[M_2A_4L_2]^{2+}$ (M = Pt(II), Pd(II); A = NH_3, (en)/2; L = amidate) have been reported, however, there is only one Pt(II)Pd(II) dimer complex of the same formula, whose crystal structure is reported.[1-6] In the present study, a novel new synthetic route to synthesize the mixed-metal dimer complex $[PtPd(bpy)_2(3,3\text{-DMGI})_2](NO_3)_2\cdot H_2O$ (**1**) from the corresponding $Pt(II)_2$ dimer $[Pt_2(bpy)_2(3,3\text{-DMGI})_2](NO_3)_2\cdot 2H_2O$ (**2**) or from the $Pd(II)_2$ dimer $[Pd_2(bpy)_2(3,3\text{-DMGI})_2](NO_3)_2\cdot 2H_2O$ (**3**) is reported. The reactions indicate novel metal substitution, in which one of the metal atoms in either **2** or **3** is replaced by $Pd(bpy)^{2+}$ or $Pt(bpy)^{2+}$ moiety, respectively, to form an identical PtPd dimer complex **1**.

Compound **2** was synthesized by reacting 1 mmol of Pt(bpy)Cl_2, 1 mmol of 3,3-dimethylglutarimide and 2 mmol of $AgNO_3$ in 25 cm^3 of H_2O. The solution was heated at 90 °C for 3 h and the resulting AgCl was removed. The filtrate was concentrated to about 1/3 and was left at 5 °C until deep violet crystals appeared.[7] Compound **3** was obtained as orange crystals in the same way as for **2** by using Pd(bpy)Cl_2 instead of Pt(bpy)Cl_2.[8] The mixed-metal dimer complex **1** was obtained by the reaction of **2** (1 mmol) with Pd(bpy)Cl_2 (1 mmol) in 25 cm^3 of H_2O. The solution was heated at 80 °C for 2 h and was concentrated to one half. After standing a few days at 5 °C, the solution gave red crystals of **1**.[9] Compound **1** can also be prepared by reacting **3** with Pt(bpy)Cl_2 instead of **2** and Pd(bpy)Cl_2 in the same way as described above. Brown crystals were obtained in this case, which, however, became red on room light irradiation. The red crystalline compound thus obtained from the photo-reaction in solid state is **1**, which was confirmed by elemental analysis, IR (KBr disk), and UV-vis (H_2O solution) spectra.

Single crystal X-ray analyses of **1**,[10] **2**,[11] and **3**[12] showed that these complexes are basically isostructural except the changes of the metal-to-metal distances. The structures of **1** and **2** are shown in Fig 1. The structure of **3** is the same as those of **1** and **2**. Although these complexes are dimers without metal-metal bondings, they form tetramers in the crystal lattices as shown in Fig 1. The central metal to metal distances are longer than 3 Å and are not considered to be metal-metal bondings. In the crystal lattice, adjacent tetramers align on a staggered line by stacking bpy ligands as shown in Fig. 2 for **2**. This sort of bpy-stacking alignment has previously been reported for $[Pt(II)_2(bpy)_2(\alpha\text{-pyrrolidonato})_2](ClO_4)_2$[6] and is also observed in the crystal lattices of **1** and **3**.

It is noteworthy that **2** reacts with $Pd(bpy)Cl_2$ to substitute one of the metals to give **1**. It is still more surprising that **3** reacts with $Pt(bpy)Cl_2$ to give the same product **1** via unknown brown crystals. The brown crystal is unstable towards X-ray irradiation and therefore X-ray crystal analysis could not be carried out. The brown crystals seem to be also a PtPd dimer complex, since the UV-vis spectra of the brown complex and **1** are identical. The reaction scheme of the metal substitution can be drawn as shown in the scheme 1. It is still unknown which of the two pathways in the scheme really occurs in the reaction, and still more puzzling is the reaction path for the reaction of **3** with $Pt(bpy)Cl_2$ to give the same product **1**.

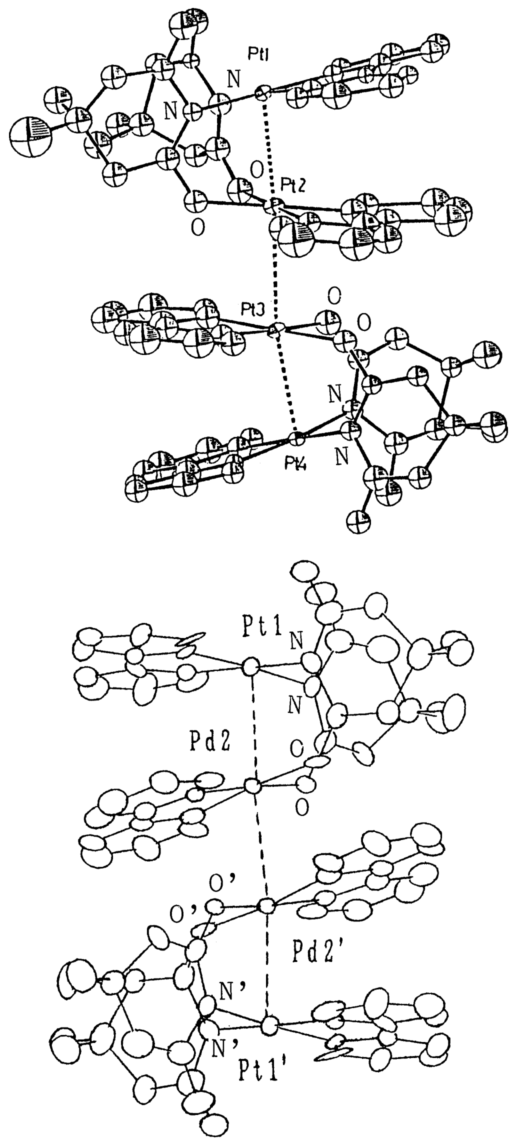


Fig. 1. Structures of $[Pt_2(bpy)_2(3,3\text{-DMGI})_2]^{2+}$ (**2**) (upper) and $[PtPd(bpy)_2(3,3\text{-DMGI})_2]^{2+}$ (**1**) (lower).

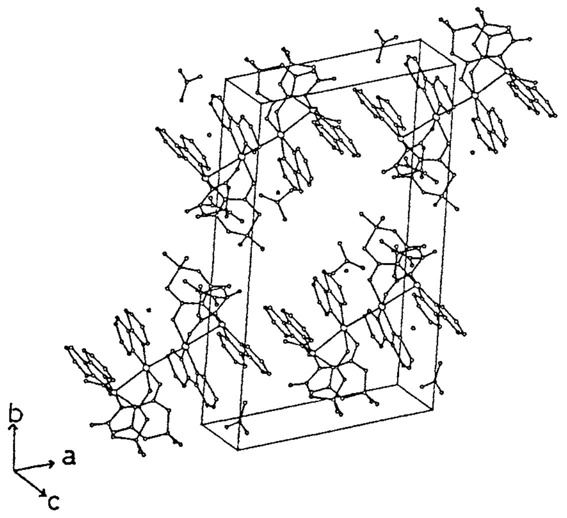


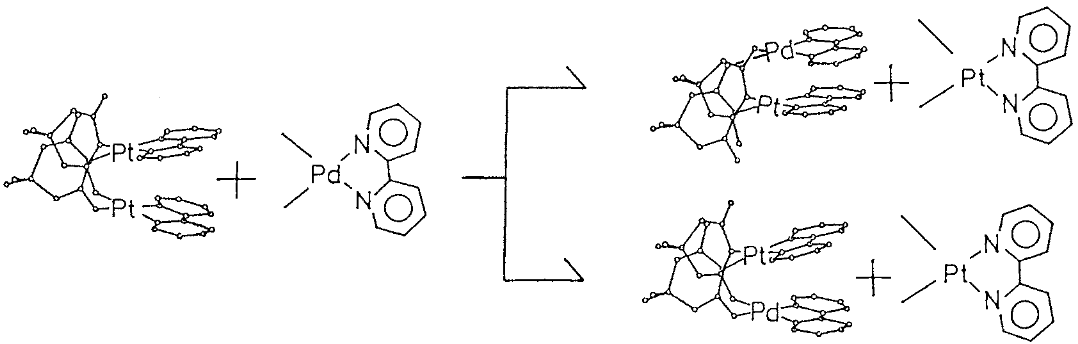
Fig. 2. Crystal structure of 2.

The major metal-to-metal distances in the dimer complexes and the UV-vis absorptions in H_2O are summarized in Table 1. It should be noted that the M_N-M'_N distances for **1** and **3** are remarkably longer than that of **2**. Although the M_N-M'_N distance of **2** is longer than metal-metal bondings observed in platinum blue complexes,[1,2] the deep violet color of **2** suggests that there is some interaction between the two platinum atoms, which is somewhat similar to platinum blue compounds and gives rise to the deep violet color.[1,2] Compound **2** is ESR silent at room temperature and liq. N_2 temperature.

Table 1. Comparison of the Structural Features and the UV-vis absorptions of $[M_OM_N(bpy)_2(3,3\text{-DMGI})_2]^{2+}$

M_O [a]	M_N [b]	Compound	Crystal color	M_O-M_N / Å	M_N-M'_N / Å	UV-vis /nm
Pt	Pt	**2**	deep violet	2.833(3) 2.845(3)	3.201(3)	474.8 307.6
Pt	Pd	**1**	red	2.854(2)	3.829(2)	412.2 307.8
Pd	Pd	**3**	orange	2.844(2)	3.849(3)	310.0

a) M_O is the metal that is coordinated by amidate-oxygen atom, i.e., the inner metal in the tetramer. b) M_N is the metal that is coordinated by amidate-nitrogen atom, i.e., the outer metal in the tetramer.



Scheme 1.

References

1) W. Micklitz, J. Riede, B. Huber, G. Müller, and B. Lippert, Inorg. Chem., 27, 1979(1989).

2) T. V. O'Halloran, P. K. Mascharak, I. D. Williams, M. M. Roberts, and S. J. Lippard, Inorg. Chem., 26, 1261(1987).

3) H. Schöllhorn, U. Thewalt, and B. Lippert, Inorg. Chim. Acta, 93, 19(1984).

4) K. Matsumoto, H. Miyamae, and H. Moriyama, Inorg. Chem., 28, 2959(1989).

5) K. Matsumoto, H. Moriyama, and K. Suzuki, Inorg. Chem., 29, 2096(1990).

6) K. Matsumoto, K. Harashima, H. Moriyama, and T. Sato, Inorg. Chim. Acta, 197, 217(1992).

7) Anal. Found: C, 35,58; H, 3.49; N, 9.95%. Calcd for $Pt_2C_{34}H_{40}N_8O_{12}$: C, 35.73; H, 3.54; N, 9.81%.

8) Anal. Found: C, 42.13; H, 4.17; N, 11.48%. Calcd for $Pd_2C_{34}H_{40}N_8O_{12}$: C, 42.29; H, 4.17; N, 11.60%.

9) Anal. Found: C, 39.61; H, 3.72; N, 10.99%. Calcd for $PtPdC_{34}H_{38}N_8O_{11}$: C, 39.40; H, 3.70; 10.82%.

10) Crystal data for $[PtPd(bpy)_2(3,3\text{-}DMGI)_2](NO_3)_2\cdot H_2O$: triclinic, space group $P\bar{1}$, $a=12.779(4)$ Å, $b=13.841(6)$ Å, $c=12.560(4)$ Å, $\alpha=100.94(4)°$, $\beta=108.42(3)°$, $\gamma=106.31(3)°$, $V=1926(1)$ Å^3, $Z=2$. A total of 4764 unique data with $F_o>4\sigma(F_o)$ in the range of $3°<2\theta<55°$ were used for the structure solution. $R=0.078$, $R_w=0.059$ $(w=1/\sigma^2(F))$. All non-hydrogen atoms were located and were anisotropically refined.

11) Crystal data for $[Pt_2(bpy)_2(3,3\text{-}DMGI)_2](NO_3)_2\cdot 2H_2O$: triclinic, space group $P\bar{1}$, $a=13.958(2)$ Å, $b=23.193(4)$ Å, $c=12.004(2)$ Å, $\alpha=92.23(1)°$, $\beta=94.40(1)°$, $\gamma=76.88(1)°$, $V=3772(1)$ Å^3, $Z=4$. A total of 4792 unique data with $F_o>4\sigma(F_o)$ in the range of $3°<2\theta<45°$ were used for the structure solution. $R=0.096$, $R_w=0.093$. Other conditions are similar to those for **1**.

12) Crystal data for $[Pd_2(bpy)_2(3,3\text{-}DMGI)_2](NO_3)_2\cdot 2H_2O$: triclinic, space group $P\bar{1}$, $a=12.754(3)$ Å, $b=13.794(3)$ Å, $c=12.591(2)$ Å, $\alpha=101.216(2)°$, $\beta=108.471(2)°$, $\gamma=106.111(2)°$, $V=1919.2(8)$ Å^3, $Z=2$. A total of 4381 unique data were used. $R=0.063$ and $R_w=0.055$. Other conditions are similar to those for **1**.

(Received August 30, 1993)