# Self-assembled Dinuclear Platinum(II) Complexes with 6,6'-Bis(1-methylbenzimidazol-2-yl)-2,2'-bipyridine: Synthesis, X-Ray Structure, and Solution Behaviors

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A novel self-assembly of two 6,6'-bis(1-methylbenzimidazol-2-yl)-2,2'-bipyridine (dmbbbpy) with two Pt(II) ions was characterized in both solid and solution states by X-ray structure analysis, $^1$H NMR and electrospray mass spectra.

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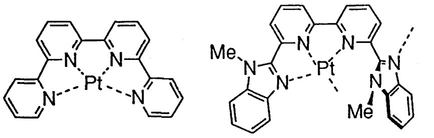
The self-assembly of supramolecular complex units based on N-heterocyclic ligands is of considerable current interest.[1] The assembled molecular architecture such as helicate is coded in the ligand donor set and in the metal ions.[1] We are interested in controlling the spatial orientation and ordering of the molecular component units. The planar structure of Pt(II) complexes makes it possible to form the well-known columnar stacks. The planar polydentate N-heterocyclic ligands such as 2,2':6',2':6',2"-quaterpyridine (qtpy), will be suited for the preferential formation of stacks arising from the additional intermolecular bond(π-stacking or donor-acceptor interactions).[2] Recently, we have synthesized new potentially tetradentate ligand, 6,6'-bis(1-methylbenzimidazol-2-yl)-2,2'-bipyridine (dmbbbpy) [3] in order to compare its coordination chemistry with that of qtpy. The qtpy ligand has several bonding modes. For example, a planar tetradentate structure of qtpy can be found in the majority of complexes containing octahedral or square-planar Ni(II),[4] Cu(II),[5] Co(III)[6] and Pt(II) ions.[7] Another mode coordinated by two bpy parts of qtpy has been reported from the reaction of qtpy and two tetrahedral Cu(I) ions to form the double helical cation $[Cu_2(qtpy)_2]^{2+}$.[8] In analogy with qtpy, we could expect that dmbbbpy adopts a planar tetradentate structure for the Pt(II) ion. However, unexpected dinuclear Pt(II) helicate complex was isolated. In this paper is described a novel self-assembly of two dmbbbpy with two Pt(II) ions.

**Scheme 1.**



$[Pt(qtpy)]^{2+}$ $[Pt_2(dmbbbpy)_2]^{4+}$

The Pt(II) complex was obtained as follows. To a hot solution of dmbbbpy (0.19 g, 0.46 mmol) in dimethyl sulfoxide (DMSO) (15 $cm^3$) was added an aqueous solution (15 $cm^3$) of $K_2PtCl_4$ (0.19 g, 0.46 mmol) under nitrogen atmosphere. The mixture was heated for 5 h, and filtered. To the filtrate $NH_4PF_6$ (1.5 g, 9.2 mmol) in water(10 $cm^3$) was added to complete the precipitation. The collected precipitate was recrystallized from DMF-methanol or acetone-methanol. Yield, 0.15 g (37%). Anal. Found C, 34.23; H, 2.72; N, 9.14%. Calcd for $C_{52}H_{40}N_{12}P_4F_{24}Pt_2$. C, 34.64; H, 2.24; N, 9.34%.

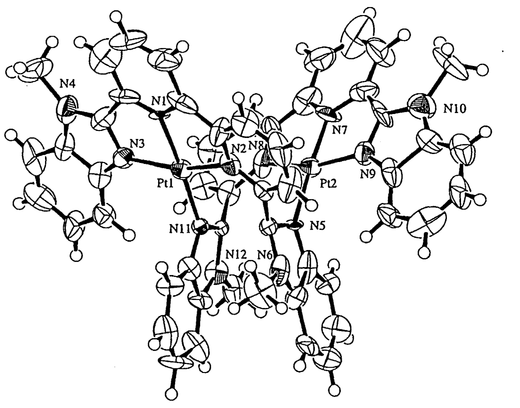


**Figure 1.** X-ray structure of the $[Pt_2(dmbbbpy)_2]^{4+}$ cation with atom-labeling scheme(hydrogen atoms are omitted). Selected structual parameters, Pt1-N1 1.92(2), Pt1-N2 2.10(2), Pt1-N3 2.06(2), Pt1-N11 2.01(2), Pt2-N5 1.99(2), Pt2-N7 1.91(2), Pt2-N8 2.08(2), Pt2-N9 1.97(2) Å, N1-Pt1-N2 82.7(9), N1-Pt1-N3 79.6(9), N1-Pt1-N11 174.9(8), N2-Pt1-N3 162.0(8), N2-Pt1-N11 102.4(8), N3-Pt1-N11 95.4(8), N5-Pt2-N7 177.0(9), N5-Pt2-N8 104.0(8), N5-Pt2-N9 96.6(8), N7-Pt2-N8 79.0(9), N7-Pt2-N9 80.3(9), N8-Pt2-N9 159.0(9)°.

The crystal structure of this Pt complex is shown in Figure 1,[9] and the selected bond lengths and angles are summarized in the figure caption. The complex cation consists of two platinum(II) ions surrounded by two tridentate dmbbbpy and linked by one of 1-methylbenzimidazolyl group in dmbbbpy each other. The Pt-N distances are all in the range expected for this type of complexes.[6] Each platinum ion adopts a distorted square-planar structure. Furthermore, the dihedral angle between two Pt planes is 114°. The Pt-Pt distance is 4.05 Å, indicating the absence of specific Pt-Pt interactions. The self-assembly of the double helical cation was formed in the crystal lattice. There is π–stacked interaction only between two 1-methylbenzimidazole rings. The present coordination mode found in Pt-dmbbbpy complex, consisting of tridentate and monodentate combination, has not been reported so far for the corresponding qtpy complexes.

In order to elucidate the solution structure of the present $[Pt_2(dmbbbpy)_2]^{4+}$, the variable-temperature $^1$H-NMR spectra in DMSO-$d_6$ were measured. At room temperature, two 1-methyl signals were observed at δ 3.87 and 4.43, as shown in Figure 2. For the ring protons, 12 sets of signals were observed while total number of ring protons is 14. The assignment of ring protons can be achieved by 2D $^1$H-$^1$H COSY NMR spectra. When the solution temperature was raised up to 150 °C, the nmr signals were simplified: i.e., one 1-methyl signal at δ 4.51 and only 5 ring proton signals were observed in spite of 7 ring protons, indicating the unfolding of the helicate structure and highly symmetrical environment around the dmbbbpy ligand. However, this nmr spectral changes cannot be explained by the simple dynamic nmr behaviors because the change of 1-methyl

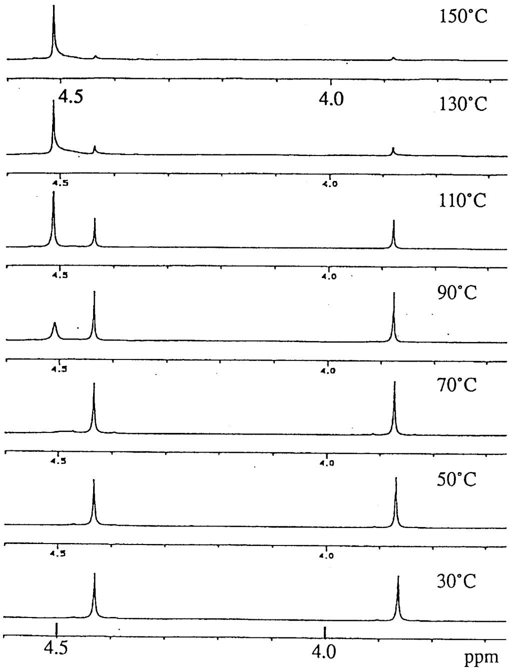


**Figure 2.** Variable-temperature $^1$H-NMR spectra(400 MHz) of [$Pt_2$(dmbbbpy)$_2$]($PF_6$)$_4$ in DMSO-$d_6$.

signal clearly indicated that simple averaging process was not involved. When the solution temperature was lowered to room temperature, the spectra was reverted slowly to the original asymmetric one ($t_{1/2}$ = ~1.5 days). These results strongly supported that the double helical structure is maintained in the solution at room temperature, but the helicate complex is unstable at higher temperature. The unfolding of double helicate by the coordination of two solvent molecules in place of 1-methylbenzimidazolyl parts of dmbbbpy may be the most probable mechanism for this temperature dependence of nmr.

The electrospray (ES) mass spectrum in $CH_3CN$ also indicates the dimer structure was held in solution. In the ES mass spectrum, the peak of nominal m/z 456, which can be assigned to [$Pt_2$(dmbbbpy)$_2$X]$^{3+}$(X = $PF_6$), was observed in addition to the peaks of m/z 306 and 756 for [$Pt_2$(dmbbbpy)$_2$]$^{4+}$ and [$Pt_2$(dmbbbpy)$_2X_2$]$^{2+}$, respectively. The former peak strongly suggested that the dinuclear structure was kept in solution, while the latter peaks could not be used to distinguish between the dinuclear and mononuclear structure because of the same m/z values. A series of small peaks were observed beside the peak of m/z 305.7 at higher m/z sides (Figure 3). These peaks were assigned to the ions [$Pt_2$(dmbbbpy)$_2$($CH_3CN$)$_n$]$^{4+}$ (n=1 ~ 6), which corresponds to the inclusion of the acetonitrile molecules in dimeric Pt complexes. This inclusion can be confirmed by the increase of the expected mass numbers when $CH_3CN$ solvent was replaced to $CD_3CN$.

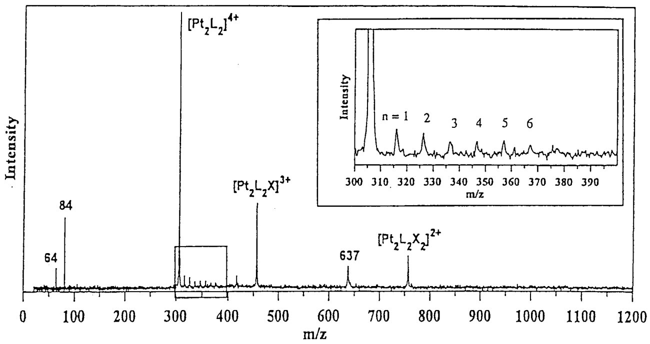


**Figure 3.** Electrospray mass spectra of [$Pt_2$(dmbbbpy)$_2$]($PF_6$)$_4$ in $CH_3CN$(0.1 mM). The inset shows the expanded spectrum which corresponds to the peaks of [$Pt_2$(dmbbbpy)$_2$($CH_3CN$)$_n$]$^{4+}$ ions.

In conclusion, the novel Pt double helicate complex was at the first time synthesized and confirmed that these structure was maintained in both solid and solution states. The different side arms between pyridine and 1-methylbenzimidazole in the 6,6'-positions of 2,2'-bipyridine will induce the steric difference, particularly for the N-N bite angle, which will be responsible for this different coordination fashion for Pt(II) ion.

## References and Notes

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9 Crystal data: $C_{52}H_{40}N_{12}F_{24}P_4Pt_2 \cdot 2DMF$, Mw = 1949.19. triclinic, $P\bar{1}$, $a$ =14.336(5), $b$ = 21.571(8), $c$ =12.366(5) Å, $\alpha$ =106.17(3), $\beta$ =105.54(3), $\gamma$ =73.45(3)°, $V$ =3445(2) Å$^3$, $Z$ =2, $D_{calc}$=1.88 g/cm$^3$, $D_{meas}$ =1.94 g/cm$^3$. $R$ = 0.086 and $R_w$ =0.093 for independent reflections. The measured density suggests the existence of more solvent molecules such as DMF, $CH_3OH$, and $H_2O$ in the crystal though they cannot be assigned from the X-ray analysis.