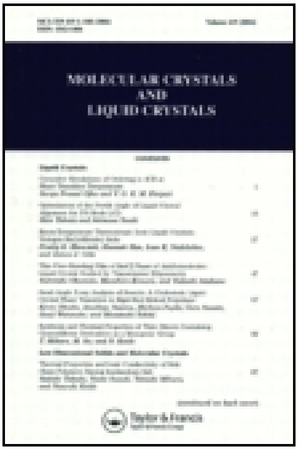

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# Bridging Ability of [Bis{2,3-di(2′-pyridyl)pyrazine}platinum(II)] and [Bis(2,2′-bipyrimidine)platinum(II)] Moieties in Polymetallic Architecture

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# Bridging Ability of [Bis{2,3-di(2'-pyridyl)pyrazine}platinum(II)] and [Bis(2,2'-bipyrimidine)platinum(II)] Moieties in Polymetallic Architecture

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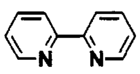
Factors influencing formation of $[\{Ru(2,2'\text{-bipyridine})_2(BL)\}_2Pt]^{6+}$ complexes, where BL are 2,2'-bipyrimidine (bpm) and 2,3-bis-(2'-pyridyl)pyrazine (dpp), were discussed in terms of π-accepting/σ-donating properties of BL and strain energies of the complexes. σ-Donation from BL to Pt(II) is crucial in formation of the $Pt(BL)_2$ type bridging moiety; pyridine provides a stronger coordination bond than pyrazine or pyrimidine, while π-back donation seems less favored. Shifts in redox potentials suggest intramolecular Ru(II) to Pt(II) charge flow through BL. Adaptable conformation is also essential in the BL structure to reduce strain upon bridging two coordination cores. High bridging ability of dpp in the polymetallic synthesis is indicated.

*Keywords:* 2,2'-bipyrimidine; 2,3-bis(2'-pyridyl)pyrazine; ruthenium complex; platinum complex; MM2 calculation

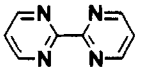
## INTRODUCTION

Assembly of functional pigments toward a well-designed structure with suitable sequence, alignment, distance and molecular interaction has been a matter of increasing attention in view of a precisely controlled photoreaction system. Such strategic assembly would be achieved by incorporating the pigments into a relatively immobile polymer backbone by a particular manner. Metal complex system would be a good backbone, since variety of functional groups can be introduced as a ligand structure so that it keeps specific orientation to a metal center.

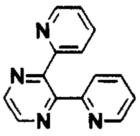
On the other, many efforts have been made to develop photocatalytic abilities of the metal complexes consisting of platinum group elements [1, 2]. Those complexes often exhibit intense absorption in visible region, high redox potential and a long-lived, emissive excited state based on the metal-to-ligand charge transfer (MLCT). Connecting hetero metal elements through α-diimine type bridging ligands (BL), we can anticipate a vectorial and sequential electron or energy transfer over the complex. As for such systems, we have been demonstrating trimetallic complexes consisting of Ru, Os, Ir, and Rh as metal elements, and 2,2'-bipyrimidine (bpm), 2,3-bis(2'-pyridyl)pyrazine (dpp), 2,3-bis(2'-pyridyl)quinoxaline and 2,3-bis(2'-pyridyl)benzoquinoxaline as BL [3-6]. Although such the $d^6$ octahedral transition metal center has been preferably used as a principal constitutional unit, consecutive connection of octahedral centers will restrict structural development of the polymetallic system. We are thus focusing on incorporation of a square planar $d^8$ center, Pt(II), to bring a variety of functioning structure and reactivity into polymetallic architecture.



**bpy**



**bpm**



**dpp**

## EXPERIMENTAL SECTION

Trimetallic complexes $[\{Ru(bpy)_2(BL)\}_2Pt]^{6+}$ (BL = bpm or dpp) were obtained by reaction between $[Pt(acetonitrile)_4]^{2+}$ and stoichiometric amount of $[Ru(bpy)_2(BL)]^{2+}$ in acetonitrile followed by the GPC purification. Details of synthesis will be published elsewhere. Augmented molecular mechanics (MM2) calculation and extended Hückel molecular orbital (EHMO) calculation were performed by the CAChe satellite program.

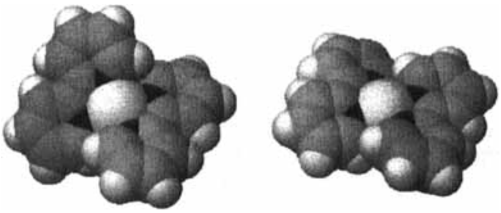
## RESULTS AND DISCUSSION

### Donor and Acceptor Property of BL

Choice of the BL is quite important in connecting two $Ru(bpy)_2$ units to $Pt(BL)_2$ moiety; dpp gave a much better yield than bpm in our trimetallic synthesis. Three factors are investigated below; electronic interaction between the metal and the ligand, structural flexibility of BL, and metal to metal distance.

α–Diimine ligands are π-electron deficient aromatics and their anti-bonding π*-orbitals can interact with *d* electrons of the central metal ion to form the characteristic π–back bonding. Degree of the metal *d* - ligand π* interaction is a function of the *d*-π* splitting energy so that the stronger π–accepting ligand (low LUMO) provides the larger interaction in the first proximity. These LUMO energies, calculated by EHMO for the structures optimized by the augmented MM2, were -10.14eV (dpp), -9.87eV (bpm) and -9.69eV (bpy). The identical series of π-accepting ability was found in their reduction potentials, -1.63 (dpp) [7], -1.80 (bpm) [8] and -2.18 (bpy) [8] (in acetonitrile, V vs. SCE). On the other, poor metal - ligand overlap (or deficient π-back donation) in (α-diimine)$PtPh_2$ complexes was argued based on their weak MLCT absorption and negative solvatochromism [9]. Strong σ-donating ligand (*e.g.*, L = $Ph^-$, $RSH^-$, $RO^-$, $R^-$ or $CN^-$) can form a stable (α-diimine)$PtL_2$ complex under such a weak π-back bonding condition [10-14]. We assume that π-back donation will be less important in the bis(α-diimine)Pt(II) type complex, since the *d*-orbital energy is lowered when two $Ph^-$ are replaced by the second α-diimine and only little overlap is anticipated between one $d_{xy}$ orbital and spatial separated two $p_x$ orbitals in the same molecular plane *y-z*. Consequently, ability of σ-donation from the ligand to the metal center should be crucial to form a stable complex. *p*Ka values of the conjugated acids are good indices of σ-donating strength of the ligands, and they are 5.17 (pyridine), 1.30 (pyrimidine) and 0.60 (pyrazine) in water [15]. The σ-donating ability is more evidential in the HOMO energy or in the Ru(II) centered oxidation potential ($E_{ox}$). σ-Donation will destabilize the HOMO and give a rise of negative shift in $E_{ox}$. $E_{ox}$ of $[Ru(bpy)_2(dpp)]^{2+}$, $[\{Ru(bpy)_2\}_2(dpp)]^{4+}$ and $[\{Ru(bpy)_2(dpp)\}_2Pt]^{6+}$ shifted -0.02V, -0.11V and -0.15V relative to the corresponding bpm complexes, respectively. This clearly indicates that bpm works as a very weak σ-donor to the second coordination event, especially when

Pt(II) occupies one side. A possible picture of the bpm bridged trimetallic complex will be an intramolecular charge transfer from Ru(II) to Pt(II) through the bpm bridge in the sequence of Ru(II)→bpm π-donation and bpm→Pt(II) σ-donation. The dpp complex may have a similar nature, but their should be enough σ-donation of dpp to the Ru(II) terminal core to neutralize the charge flow.



(a) (b)

FIGURE 1 Configurational isomers of $[Pt(bpy)_2]^{2+}$, twisted (a) and bent (b).

Structural Issues of Bridging Ligands in Polymetallic Architecture

In the square planar $[Pt(bpy)_2]^{2+}$ complex (figure 1), Van der Waals repulsion between two pairs of facing 6(6')-H of pyridine will result in twisting two ligands towards a tetrahedral geometry (a) or bending each ligand (b) [16]. The most stable structure is found in the twisted configuration (a) from the MM2 calculation; the optimized energy of (a) is 8.6 kcal/mol lower than that of (b). The MM2 optimization was carried out for all the trimetallic complexes including configurational isomers, *i.e.* 8 and 16 isomers for bpm and dpp, respectively. Results are shown in the table-1. We here used $\delta$ or $\lambda$ to denote the twist of Pt(II) square plane; *e.g.* (a) is in the $\delta$ form. Our calculation revealed that (i) the final energy of the trimetallic complex is nearly insensitive to the absolute configuration, but (ii) it apparently increases along with the molecular size (*i.e.* the number of atoms involved). These are rather reasonable when the total energy is mainly controlled by the atom-atom interaction (Van der Waals and electrostatic interaction). Interestingly, however, the reverse order is seen in the bond stretch strain, in the bond angle strain and in the dihedral angle strain. These strain energies of the bpm complexes are higher than those of the dpp complexes. The difference can be ascribed to the structural rigidity of BL (figure 2). Two pyrimidines in a bridged bpm are almost coplanar (the dihedral angle N1-C2-C2'-N1' is 0-0.3°), while two pyridines in a bridged dpp are tilted 12-13° relative to pyrazine to have a strain-free conformation. As a result, the bond angle C6-N1-metal is forced to 130±1° in the bpm complexes, while it is 122±1° in the dpp complexes being equivalent to the natural angle of the $sp^2$ hybridization. The calculated angle strain of C6-N1-Pt(II) is ~6.0 kcal/mol in the bpm system which is more than twice of the dpp system (~2.4 kcal/mol) and exceeds the cyclobutane's C-C-C angle strain (3.82kcal/mol). The Ru(II)-Pt(II) distance also differs in two BL systems; 5.39Å in the bpm system and 6.71Å in the dpp system. The large constraint and the large Coulombic repulsion could be obstacle in building up the polymetalic complex.

TABLE 1
Augmented MM2 energies of Ru(II) - Pt(II) complexes (kcal/mol).

| Compound | Bond Stretch | Bond Angle | Di-hedral | Van der Waals | Electro-statics | Final Energy |
|---|---|---|---|---|---|---|
| $[Ru(bpy)_2(bpm)]^{2+}$ | 0.46 | 32.11 | -44.94 | 7.99 | -36.03 | -40.35 |
| $[Ru(bpy)_2(dpp)]^{2+}$ | 0.71 | 33.44 | -53.08 | 10.57 | -25.25 | -33.48 |
| $\Delta,\Delta,\delta$–<br>$[\{Ru(bpy)_2(bpm)\}_2Pt]^{6+}$ | 2.41 | 103.50 | -89.14 | 10.53 | -80.64 | -53.43 |
| $\Delta,\Delta,\delta$–*E*-<br>$[\{Ru(bpy)_2(dpp)\}_2Pt]^{6+}$ | 1.75 | 97.51 | -99.82 | 21.97 | -50.81 | -28.76 |
| $\Delta,\Delta,\delta$–*Z*-<br>$[\{Ru(bpy)_2(dpp)\}_2Pt]^{6+}$ | 1.81 | 97.97 | -99.86 | 22.01 | -50.42 | -27.88 |

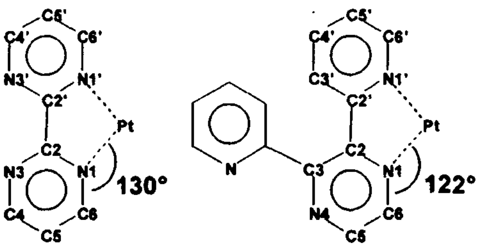


FIGURE 2 Bond angles C6-N1-Pt of bpm and dpp upon coordination.

## CONCLUSION

Square planar $Pt(BL)_2$ can be incorporated between octahedral $Ru(bpy)_2$ moieties. BLs with strong σ-donation and adaptable conformation are favorable for the $Pt(BL)_2$ bridging function.

Acknowledgements

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