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U– to Z–shape isomerization in Pt₂Ag₂ framework containing pyridyl-NHC ligands

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Synthesis and isomerization of heteropolynuclear Pt₂Ag₂ complex containing pyridyl N-heterocyclic carbene (NHC) ligands are reported. The Pt₂Ag₂ complex could take two geometrical isomers possessing twisted U-shaped structure and Z-shaped structure. The rate of isomerization reaction depended on the concentration of the solution, implying that the reaction took place through an intermolecular process.

Metal–metal interactions have been increasingly recognized as a powerful tool to construct supramolecular and crystal engineering systems. In particular, metal–metal interactions among different metal atoms are expected to show characteristic features owing to their cooperative effects, giving unique structures, reactivities, and properties. For example, bimetallic interactions in cooperative catalysis offer the unique advantage of metal centers accompanying different nature in close proximity, leading to a significant molecular activation that individual mononuclear complexes cannot achieve.

Furthermore, structures and photophysical properties of heteropolynuclear complexes involving metal–metal interactions, such as Pt complexes containing group 11 metal ions, have also been widely investigated. Some of heteropolynuclear complexes having metal–metal interactions also show unique molecular rearrangements in solution, owing to their weak bonding nature.

We have revealed the structures and luminescent properties of heteropolynuclear complexes having various extent of multiple metal–metal interactions. For example, [(ppy)Pt₂Ag₂(μ-Me₂pz)₂] (ppy = 2-phenylpyridine and Me₂pz = 3,5-dimethylpyrazolate) and [(bpy)Pt₂M₂(μ-Me₂pz)₄] (PF₆)₂ (M = Au, Ag and bpy = 2,2'-bipyridine) exist as a mixture of U- and Z-shaped isomers in solution, respectively, whose luminescent properties are almost independent on the incorporated group 11 metal ions. Furthermore, U-shaped isomer showed reversible trapping of Ag ion within a U-shaped cavity via multiple metal–metal interactions. Although various properties of heteropolynuclear complexes have been investigated by using a variety of C^N chelate ligands represented by ppy and its derivatives, those of heteropolynuclear complexes involving N-heterocyclic carbene (NHC) ligands have not been fully explored.

Furthermore, structural isomerization involving rearrangement of complex framework such as that between U- and Z-shaped structures is still unclear. Herein we report the synthesis, structure, isomerization and emission properties of pyrazolato-bridged Pt₂Ag₂ complexes having pyridyl-NHC chelate ligand. The pyridyl-NHC ligand works as a neutral C^N chelate ligands similarly to N^N chelate ligands (e.g. bipyridines) and has unique electron donating character on the carbene moiety. The strong s-donor property of the NHC ligands was expected to raise the d-d transition energy effectively, resulting in a higher energy emission from the complexes. In this paper, we also elucidated the nature of pyridyl-NHC ligand as a neutral C^N chelate ligand in the Pt₂Ag₂ system.

The pyrazolato-bridged Pt₂Ag₂ complex 3 was synthesized from the mononuclear Pt(II) complex 1 in a similar manner to our previous methods (Scheme 1). The dimethylpyrazolato complex [(Py-NHC)Pt(Me₂pzH)](PF₆)₂ (2) was obtained by the reaction of [(Py-NHC)PtCl₂] (1) with Me₂pzH in the presence of AgPF₆ in CH₃CN in 75% yield. The formation of [2](PF₆)₂ was confirmed by ESI-MS and single crystal X-ray diffraction. The dimethylpyrazolato complex 2 was treated with AgPF₆ under similar conditions to give a yellow mixture of two isomers 3 andScheme 1 Synthesis of Heteropolynuclear Pt₂Ag₂ Complex [3](PF₆)₂

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The intermolecular metal interactions in [\(\text{Pt} \cdot \cdot \cdot \text{Pt}\)] Å, Ag: 1.65 Å, suggest than the sum of the van der Waals radius of the metal atoms (Pt: 1.77 Å, Ag: 1.65 Å) in [\(\text{Pt} \cdot \cdot \cdot \text{Pt}\)] Å, Ag: 1.65 Å, suggests that CH···N interaction in the solid state (Fig. S11†). In contrast, the complex cations and the counter anions were alternately oriented in the crystal, indicating no intermolecular metal···metal interaction in the solid state (Fig. S11†). The Pt–N(pyrazolato) bond distances at trans position of NHC moieties are approximately 0.05 Å longer than those at trans position of pyridine rings. The difference is attributed to the stronger trans influence of NHC moiety than that of pyridine moiety.

The NMR studies revealed that the U-shaped Pt2Ag2 complex [\(\text{Pt} \cdot \cdot \cdot \text{Pt}\)] showed isomerization in the solution, although multiple metal···metal interactions were observed in the crystal structure (Fig. 3a). When the single crystal of the U-shaped isomer [\(\text{Pt} \cdot \cdot \cdot \text{Pt}\)] was dissolved in CD3CN, new sets of signals appeared within 5 min and their intensities gradually increased (Fig. S6†). The signals assigned to pyridine protons were observed around a downfield region compared with those of [\(\text{Pt} \cdot \cdot \cdot \text{Pt}\)] but not stacked each other. This behavior is very similar to those of Pt2Ag2 analogues, which exist as a mixture of U- and Z-shaped complexes in the solution.54 Thus the new sets of signals in the 1H NMR spectrum were assigned to the Z-shaped isomer [\(\text{Pt} \cdot \cdot \cdot \text{Pt}\)] and [\(\text{Pt} \cdot \cdot \cdot \text{Pt}\)]. The integral ratios of the signals reached U:Z = 2:1 in a thermodynamic equilibrium state (Fig. 3b). These results suggest that the metal···metal interactions and Ag···N(pyrazolato) bonds in [\(\text{Pt} \cdot \cdot \cdot \text{Pt}\)] are actually labile in solution. The U-shaped isomer is thermodynamically favored one as evidenced by the integral ratio of U:Z in 1H NMR spectra, probably because the highly twisted U-shaped structure can induce the short contacts among the Pt and Ag ions to endow effective thermodynamic stability by metal···metal interaction. These two sets of signals for [\(\text{Pt} \cdot \cdot \cdot \text{Pt}\)] and [\(\text{Pt} \cdot \cdot \cdot \text{Pt}\)] were also observed in the crude reaction product (Fig. S8†). Thus, the U-shaped isomer [\(\text{Pt} \cdot \cdot \cdot \text{Pt}\)] is selectively crystallized via isomerization in the crystallization process. It is noteworthy here that the isomerization rate became slow in a diluted condition, indicating that the reaction took place through an intermolecular process (Fig. 3b). Additionally, the isomerization reaction immediately reached a state of thermodynamic equilibrium when single crystals of the U-shaped isomer [\(\text{Pt} \cdot \cdot \cdot \text{Pt}\)] was dissolved in coordinating solvent, such as CD3CN. It implies that isomerization was accelerated by the coordination of solvent molecules to the Ag ions, which was competed with that of Me2pz ligands. The VT-NMR spectra of [\(\text{Pt} \cdot \cdot \cdot \text{Pt}\)] (i.e. the mixture of [\(\text{Pt} \cdot \cdot \cdot \text{Pt}\)] and [\(\text{Pt} \cdot \cdot \cdot \text{Pt}\)])in the state of thermodynamic equilibrium) recorded even at

**Fig. 1** 1H NMR spectra (500 MHz, r.t.) of (a) 1 in DMSO-d6, (b) [\(\text{Pt} \cdot \cdot \cdot \text{Pt}\)] consisting of two geometrical isomers in CD3CN and (c) U-shaped Pt2Ag2 complex [\(\text{Pt} \cdot \cdot \cdot \text{Pt}\)] in CD3CN.

**Fig. 2** ORTEP representation (50% probability ellipsoids) of U-shaped Pt2Ag2 complex cation [\(\text{Pt} \cdot \cdot \cdot \text{Pt}\)] (left side view, right) viewed along the Pt···Pt axis. Hydrogen atoms and methyl groups are omitted for clarity. Selected bond lengths (Å): Pt1···Pt2 5.3613(5), Pt1···Ag1 3.1537(5), Pt1···Ag2 3.5849(6), Pt1···N21 1.998(3), Pt1···N31 2.053(3), Pt2···Ag1 3.6208(5), Pt2···Ag2 3.1885(5), Pt2···N51 2.001(3), Pt2···N61 2.050(3), Ag1···Ag2 3.0745(5).
The lack of argentophilic interactions, which overcomes the electrostatic framework via multiple metal complexes, strongly suggests that a dicationic chelate ligand plays an important role for the capturing of Ag(I) ion in solution. However, the formation of Pt

313 K in CDCl₃ and CD₂CN showed no coalescence of signals, indicating that isomerization between U- and Z-shaped structure is slow process and does not proceed in the NMR time scale (Fig. S7f).

We recently reported that U-shaped Pt₂Ag₂ complexes having C≡N chelate ligands can show reversible entrapment of Ag(I) ion in the Pt₂Ag₂ framework through Ag···Ag interaction and the formation of Pt→Ag dative bonds. Therefore, the U-shaped Pt₂Ag₂ structure of [3]([PF₆]₂) encouraged us to elucidate a binding ability for Ag(I) ion in solution. However, the ¹H NMR spectrum of [3] did not change even by the addition of the excess amount of Ag(I) ion into the solution, indicating that the U-shaped Pt₂Ag₂ complex [3] cannot stabilize additional Ag(I) ion in the Pt₂Ag₂ framework via multiple metal–metal interactions (Fig. S9f). On the other hand, Miguel recently reported that a dicatonic [Ag₂(bisNHC)₂]²⁻ complex captures even cationic [Ag(NCCH₃)₂]⁺ guest in the molecular cavity of Ag₂ framework via strong argentophilic interactions, which overcomes the electrostatic repulsion between the complex cation and Ag ion. These results strongly suggest that a π-coordination ability of C(ipso) atom in the C≡N chelate ligand plays an important role for the capturing of Ag(I) ion into the Pt₂Ag₂ systems through Ag-C(ipso) bonding interaction. The lack of π-coordination ability of the carbene carbon atom in Py-NHC ligand is attributed to the insensitive behavior of [3] toward Ag(I) ion.

![Schematic representation of the isomerization from U-shaped isomer [3]([PF₆]₂) to Z-shaped isomer [3]([PF₆]₂).](image)

Fig. 4 UV-Vis absorption spectra (red of [2][PF₆]₂) and [3][PF₆]₂) solid line) in CH₂CN and their normalized emission spectra (blue) in the solid state at room temperature (λ_{ex} = 355 nm).

The mononuclear Pt(II) complex [2][PF₆]₂ and Pt₂Ag₂ complex [3][PF₆]₂ showed the lowest energy absorption bands at 320 nm (sh) and 335 nm, respectively, in CH₂CN at room temperature, whose energies are higher than those of Pt₂Ag₂ analogue having ppy chelate ligands (Fig. 4). Since the corresponding absorption band is absent in [2][PF₆]₂, the band at 335 nm in [3][PF₆]₂ is originated from the formation of Pt₂Ag₂ structure.

Although the complexes [2][PF₆]₂ and [3][PF₆]₂ did not display photoluminescence in solution at room temperature, they showed structured emission spectrum (λ_{max} = 431 nm) and broad one (λ_{max} = 507 nm), respectively, in the solid state (Fig. 4). The observed lifetimes of the emission in few hundreds of nanoseconds indicate that the emissions are phosphorescence (Table S1f). Corresponding to the appearance of lower energy absorption bands in [3][PF₆]₂, the emission bands of [3][PF₆]₂ significantly red-shifted (Δλ_{max} = +76 nm) compared with those of [2][PF₆]₂, indicating that the incorporation of Ag(I) ions drastically affects the emission energy. To our surprise, the emission quantum yield (Φ) of [3][PF₆]₂ (1%) was smaller than that of [2][PF₆]₂ at room temperature. This is in contrast to our previous results that the formation of mixed-metal complexes having multiple metal–metal interactions affords brighter luminescence than the precursor Pt(II) complex in the solid states.

To unveil the origin of the differences in photophysical properties between [2][PF₆]₂ and [3][PF₆]₂, the time dependent density functional theory (TD-DFT) method were investigated. The DFT calculation clearly visualized the highest-occupied molecular orbitals (HOMOs) and lowest-unoccupied molecular orbitals (LUMOs) in the complexes (Tables S3–S6, Fig. S13 and S14f). LUMOs of the both complexes are similar to each other and consisting of the π* orbital of pyridyl moiety, while HOMOs are consisting of π orbital of Me₂pz moieties and 5d orbital of Pt atom. Moreover, large contribution of 4d orbital of Ag atoms is found in HOMO-2 of [3][PF₆]₂. These calculations suggest that the lowest energy
absorption bands of $[2](PF_6)_2$ can be assigned mainly to the combination of ligand-to-ligand charge transfer (LLCT) [$\pi^*$(Py-NHC)] and metal-to-ligand charge transfer (MLCT) [$\pi^*$(Py-NHC)] transitions. The assignment for $[3](PF_6)_2$ is essentially very similar to that of $[2](PF_6)_2$. However, in addition to the combination of LLCT and MLCT transitions, the metal-to-ligand charge transfer (M’LCT) [$\pi$→$\pi^*$(Py-NHC)] transitions further contribute to the lowest energy absorption band in $[3](PF_6)_2$ due to the formation of Pt$_2$Ag$_2$ complex. The features of emission spectra of $[2](PF_6)_2$ and $[3](PF_6)_2$ may be attributed to the different nature of their excited states (Tables S5 and S6).

Conclusions

In summary, we synthesized the heteropolynuclear Pt$_3$Ag$_2$ complex having pyridyl-NHC chelating ligands with multiple Pt–Ag and Ag–Ag interactions. Although the as-prepared Pt$_3$Ag$_2$ complex exists as a mixture of two isomers, it selectively crystallized to afford only U-shaped isomer in the solid state, allowing us to elucidate the thermodynamically favored isomer as well as the U to Z structural isomerization in solution. The Pt$_3$Ag$_2$ complex having pyridyl-NHC chelating ligands showed higher emission energy than the Pt$_3$Ag$_2$ analogues having other aromatic C=N chelate ligands like 2-phenylpyridine derivatives. This is probably due to the strong donating ability of carbene carbon atom on the Py-NHC ligand. These results give us new insights into the relationship between structural transformations and photophysical properties involving weak intramolecular metal–metal interactions, leading to a construction of new types of functional molecules incorporating both dynamic molecular systems and light-emitting properties.

Conflicts of interest

There are no conflicts to declare.

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Notes and references


