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Synthesis of the First Platinum Blue Complex with 2,2'-Bipyridine as the Amine Ligand and Its Aqueous Solution Behavior

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Synthesis of the first platinum blue complex with 2,2'-bipyridine ligand, $[Pt_4(bpy)_4(GI)_4]^{5+}$ (bpy = 2,2'-bipyridine; GI = glutarimidate) and its solution behavior are reported.

All the platinum blue complexes of a general formula $[Pt(II)_3Pt(III)A_8L_4]^{5+}$ (A = NH_3 or (ethylenediamine)/2; L = amidate anion) so far reported have either NH_3 or ethylenediamine (en) as the amine ligand A. It has been believed that the bpy analogue $[Pt(II)_3Pt(III)(bpy)_4L_4]^{5+}$ can not be prepared at least under the analogous synthetic conditions, because bpy's electron accepting nature from the metal to the π^* orbital of bpy decreases the electron density on the Pt atoms.[1,2] Since the platinum atoms in the precursor of the blue complex, $[Pt(II)_2(bpy)_2L_2]^{2+}$, are electron-poorer, compared to those in the analogous NH_3 or en complexes, the redox potentials of the bpy complexes are higher than those of the latter complexes. As a result, the bpy precursors are not oxidized to the corresponding tetranuclear blue complexes.[1,2] In the present study, we prepared the first platinum blue complex with bpy ligand $[Pt(III)Pt(II)_3(bpy)_4(GI)_4](NO_3)_5 \cdot 2H_2O$ (**1**), together with its reduced form HH (head-to-head)-$[Pt(II)_2(bpy)_2(GI)_2](NO_3)_2 \cdot 3.5H_2O$ (**2**).

Violet crystals of **2** were prepared similarly to the previously reported analogous complex, HH-$[Pt(II)_2(bpy)_2(3,3\text{-DMGI})_2](NO_3)_2 \cdot 2H_2O$[3] (3,3-DMGI = 3,3-dimethylglutarimidate), by using glutarimide instead of 3,3-dimethylglutarimide.[4] Compound **1** was prepared by reacting 1 mmol of $Pt(bpy)Cl_2$, 1 mmol of glutarimide and 2 mmol of $AgNO_3$ in 25 cm^3 of H_2O. After heating the solution at 90 ℃ for 3 h, 1 mmol of $Pd(bpy)Cl_2$ and 2 mmol of $AgNO_3$ were added. The solution was heated at 90 ℃ for another 2 h, and then the resulting AgCl was removed. The filtrate was concentrated to one third and 0.4 cm^3 of conc. HNO_3 was added. After standing at room temperature for a few days, the solution gave dark violet crystals of **1**.[5]

Compound **1** was also prepared by using Pt(bpy)Cl_2 instead of Pd(bpy)Cl_2 in the above method, but the former method gives better reproducibility. These preparative methods correspond to the oxidation of in situ prepared HH-$[Pt(II)Pd(II)(bpy)_2(GI)_2]^{2+}$ (the former method)$^{3)}$ or of **2** (the latter method)$^{3)}$ by conc. HNO_3, but why oxidation of $[PtPd(bpy)_2(GI)_2]^{2+}$ gives the platinum blue complex **1** remains still unexplained. Compound **1** is paramagnetic, whose aqueous solution ESR spectrum shows an axial pattern with $g_{\parallel} = 2.000$ and $g_{\perp} = 2.40$ at room temperature.

The UV-vis spectrum of Compound **1** in H_2O exhibits absorption maxima at 781.0, 583.8 and 307.6 nm, which however gradually disappear. After a few hours, the compound is reduced by H_2O to compound **2**. This sort of reduction in water is already known for other platinum blue complexes with NH_3 as the amine ligand.$^{6,7)}$ The reduction of **1** to **2** was confirmed by the UV-vis spectrum (λ_{max} for **2** in H_2O is 474.3 nm). Compound **2** is also unstable in H_2O and its spectrum again changes. The latter change was also monitored with ^{195}Pt and ^{13}C NMR spectroscopy. Since the reaction is very slow at room temperature ($\approx$ a month for completion), the ^{195}Pt spectrum shown in Fig. 1B was measured at room temperature after the reaction had been accelerated by heating at 65 ℃ for 3.5 h. By this treatment, the solution gave yellow precipitate, which was confirmed by IR spectroscopy and elemental analysis to be hydroxide-bridged dimer, $[Pt(II)_2(bpy)_2(\mu\text{-}OH)_2](NO_3)_2$.$^{8)}$ The spectrum of Fig. 1A shows that **2** is a head-to-head (HH) isomer (Scheme 1) with the peaks at -1429 and -2224 ppm, while Fig. 1B shows that **2** is changed to another species. In order to assign the new ^{195}Pt peaks in Fig. 1B, ^{13}C NMR spectrum of the same solution was measured (Fig. 2). In Fig. 2, the peaks with * appear even just after dissolution, suggesting these are the HH isomer. The peaks with ○ correspond to free glutarimide ligand. The peak pattern of ● is very similar to that of the peaks with *; each ● peak is located very close to one

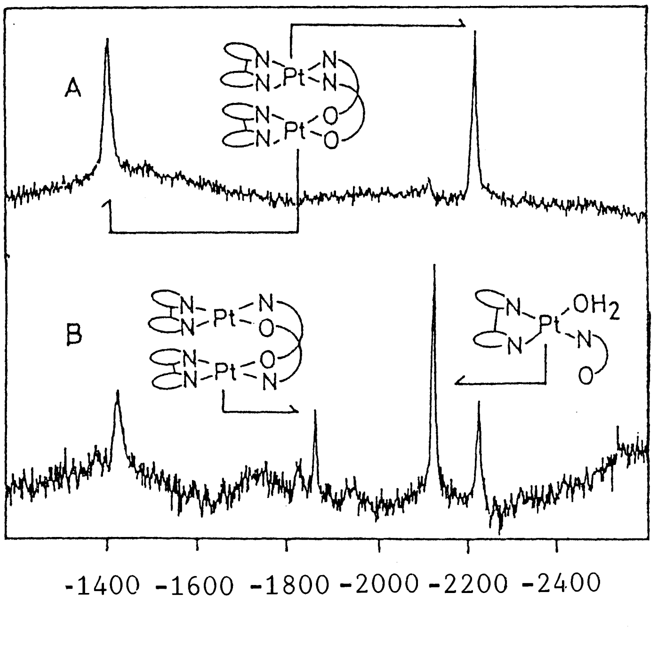
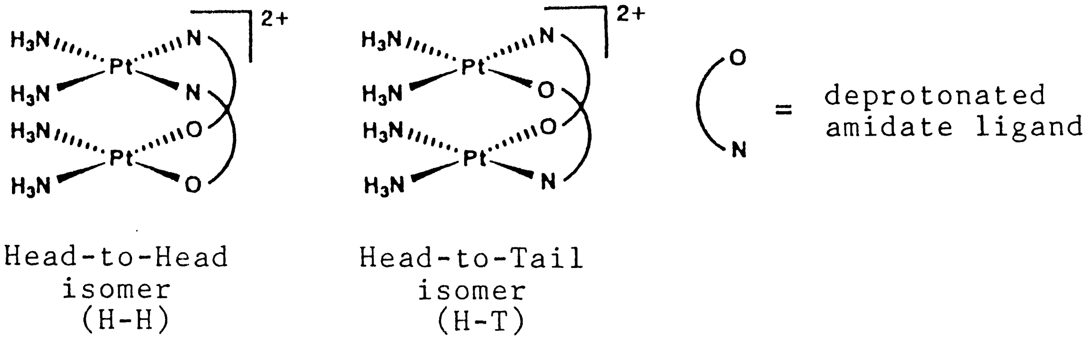


Fig. 1. ^{195}Pt NMR spectra of **2** in D_2O. The chemical shift is relative to K_2PtCl_4 as -1616.483 ppm. A, just after dissolution; B, after heating at 65 ℃ for 3.5 h.



Scheme 1.

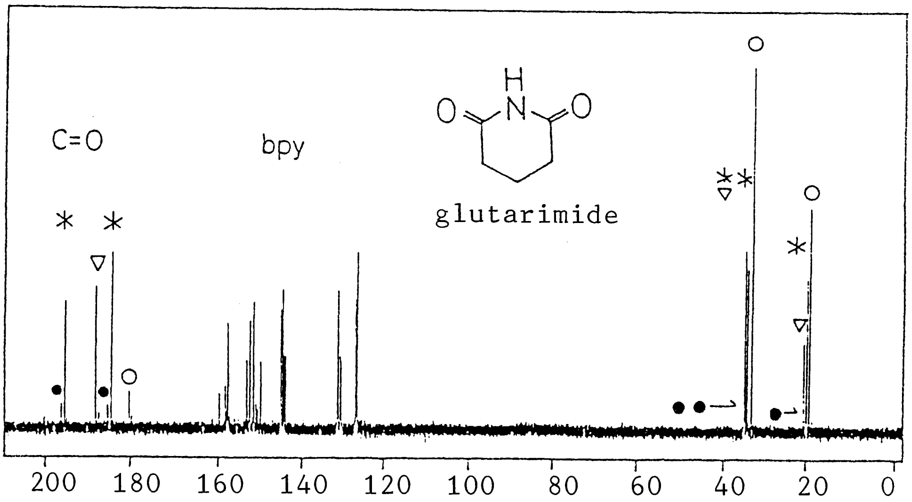
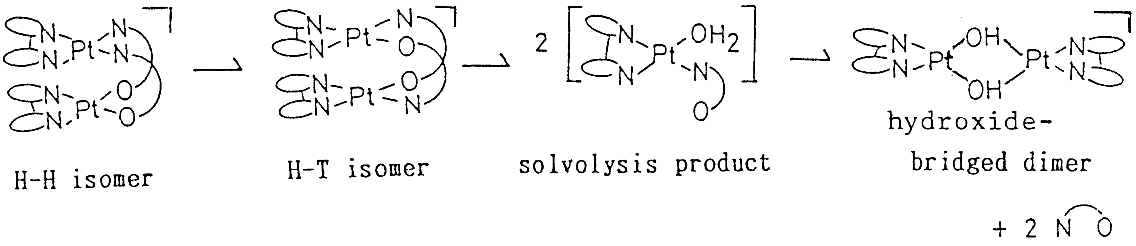


Fig. 2. ^{13}C NMR spectra of the same solution with Fig.1B. The chemical shift is relative to TMS. For the definitions of the marks, see the text.

of the * peaks, suggesting that ● corresponds to the head-to-tail (HT) isomer as already observed in ^{13}C and ^{1}H NMR spectra of several other amidate-bridged Pt(II) or Pd(II) dimer complexes of a formula $[M_2(NH_3)_4L_2]^{2+}$ (M = Pt(II) or Pd(II), L is amidate).[6,9] This assignment is also supported by the Pt spectrum (Fig. 1B), if one considers that the new peak at -1860 ppm corresponds to the ^{13}C ● peaks, and that the ^{195}Pt peak of a HT isomer always lies at about the avarage value of the two chemical shifts for the HH isomer.[6,10] The peaks with ▽ in Fig. 2 suggest that this GI ligand coordinates to the Pt atom only with its N atom, since the carbonyl chemical shift is down-field shifted by 8 ppm, compared with free glutarimide, and such shift is similar to what we observed previously for cis-$[Pt(II)(NH_3)_2(3,3\text{-DMGI})(H_2O)]^+$, which is produced from the hydrolysis of HT-$[Pt(II)_2(NH_3)_4(3,3\text{-DMGI})_2]^{2+}$.[7,11] The peaks with ▽ in Fig. 2 and the new ^{195}Pt peak at -2120 ppm (Fig. 1B) are therefore assigned to $[Pt(II)(bpy)_2(GI)(H_2O)]^+$, and the total reaction scheme can be drawn as shown in Scheme 2. The major difference in the reactions of the previously reported HT-[Pt(II)$_2$(NH$_3$)$_4$(3,3-DMGI)$_2$]$^{2+}$ and the present compound HT-[Pt(II)$_2$(bpy)$_2$(GI)$_2$]$^{2+}$ is that only the monomeric complex cis-[Pt(II)(NH$_3$)$_2$(3,3-DMGI)(H$_2$O)]$^+$ is produced from the former complex, while the analogous monomeric complex further undergoes hydrolysis to precipitate the hydroxide-bridged dimer complex in the present case.



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4) Anal. Found: C, 32.15; H, 2.97; N, 10.29%. Calcd for $Pt_2C_{30}H_{35}N_8O_{13.5}$: C, 32.35; H, 3.17; N, 10.06%.
5) Anal. Found: C, 32.57; H, 2.73; N, 10.86%. Calcd for $Pt_4C_{60}H_{60}N_{17}O_{25}$: C, 32.76; H, 2.76; N, 10.83%.
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