complex, with an intense exciton-derived CD absorption consistent with retention of the *R* configuration of the binaphtholate ligand at 231 nm.

The new (binaphtholate)W_2(O-*t*-Bu)$_4$ complexes react readily with acetylenes and other unsaturated organic substrates, and studies of the structures of these products and stereoselectivity of the reactions are currently under investigation.

Supplementary Material Available: Tables of fractional coordinates and isotropic thermal parameters, anisotropic thermal parameters, bond distances, and bond angles and a summary of crystallographic data for 1,2-[3,3′-Me$_2$-1,1′-(OC$_{10}$H$_5$)$_2$]W$_2$(O-*t*-Bu)$_4$ (8 pages); table of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

Correlation between the Optical Transitions and Metal–Metal Vibrational Frequencies in Pt$_4$$^{9+}$ Cations: A Resonance Raman Study

Hans K. Mahtani[1] and Paul Stein*

*Department of Chemistry, Duquesne University
Pittsburgh, Pennsylvania 15282*

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Mixed-valent-state platinum and dinuclear Pt^{III} complexes with bridging amidate ligands have been reported at an accelerated pace.[2-6] Their Pt–Pt bonding continues to attract attention.[7] Three mixed-valent-state platinum complexes have been characterized by X-ray crystallography and shown to contain structurally similar Pt$_4$$^{9+}$ cations. The *cis*-diammineplatinum α-pyridone blue cation,[4] Pt$_4$(NH$_3$)$_8$(C$_5$H$_4$NO)$_4$$^{5+}$ (**1**), and the *cis*-diammineplatinum 1-methyluracil blue cation,[5] Pt$_4$(NH$_3$)$_8$-(C$_5$H$_5$N$_2$O$_2$)$_4$$^{5+}$ (**2**), consist of two amidate-bridged dimers of *cis*-diammineplatinum with the exocyclic oxygens coordinated to the inner platinum atoms, Pt2 and Pt2′, as schematically shown:
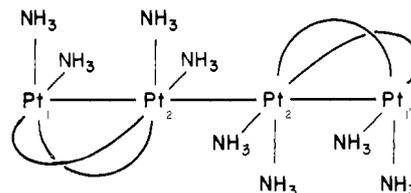
The (ethylenediamine)platinum α-pyridone blue cation, Pt$_4$-(en)$_4$(C$_5$H$_4$NO)$_4$$^{5+}$ (**3**), is similar to **1**, with *cis*-diammine replaced by ethylenediamine (en) ligands.[6] In this communication we present resonance Raman (rR) spectra of the Pt$_4$$^{9+}$ cations in aqueous solution and establish a relationship between the two principal optical absorptions and the Pt–Pt vibrational frequencies. The results provide a benchmark for the study of similar platinum clusters, such as the platinum pyrimidine blues.[8]

The rR spectrum of **1** consists of two intense bands due to an interdimer Pt–Pt stretch, ν(Pt2–Pt2′) = 69 cm^{-1}, and an intradimer Pt–Pt stretch, ν(Pt1–Pt2) = 149 cm^{-1}.[9] ν(Pt2–Pt2′) results from the oscillation between the two dimer units as a whole and is a measure of the Pt2–Pt2′ bonding (with an estimated force constant for 0.4 ± 0.1 mdyn/Å) as well as N–H$\cdots$O interdimer hydrogen bonding. ν(Pt1–Pt2), which contains a significant contribution from the bridging α-pyridonate ligands, is comparable with ν-(Pt–Pt) = 170–184 cm^{-1}, observed for bis(*cis*-diammineplatinum(III)) complexes with two bridging α-pyridonate ligands, and ν(Pt–Pt) = 140 cm^{-1}, observed for a corresponding diplatinum(II) complex.[12] The good inverse correlation of the Pt–Pt distances, 2.53–2.57 Å^{3c,d} for Pt^{III}$_2$, 2.89 Å^{13} for Pt^{II}$_2$ complexes, and 2.774 Å for Pt1–Pt2 in **1**, with ν(Pt–Pt) confirms the assignment of ν(Pt1–Pt2). A bond order of 0.2 is estimated for Pt1–Pt2 from ν(Pt–Pt) assuming bond orders of 1 and 0 for the Pt^{III}$_2$ and Pt^{II}$_2$ complexes, respectively. Thus the Pt2–Pt2′ and Pt1–Pt2 bonding is nearly equivalent and consistent with previous reports[14,15] that the unpaired electron in **1** is delocalized over the Pt$_4$$^{9+}$ chain.[16] A structurally similar Pt$_4$$^{10+}$ cation, *cis*-diammineplatinum α-pyrrolidone tan, shows a rR spectrum[17] having

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(9) The rR experiments were performed with a 1404 Spex monochromator, a Spectra-Physics 165 krypton ion laser, and an IBM 9000 microcomputer. Data were digitally collected at 0.5-cm^{-1} increments. The rR spectra were obtained by flowing the sample solution through a 1-mm glass capillary tube with a peristaltic pump and silicone tubing. A reservoir was installed in the loop where the samples were maintained near 0 °C using an ice bath. The Pt$_4$$^{9+}$ samples were verified by their optical absorption spectra, which were typically measured before and after the rR experiments.

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(16) The rR band widths of ν(Pt2–Pt2′) ($\sim$13 cm^{-1}) and ν(Pt1–Pt2) ($\sim$18 cm^{-1}) are large compared with those of ν(Pt–Pt) ($\sim$5 cm^{-1}) observed for Pt^{II} and Pt^{III} binuclear complexes with bridging μ-pyrophosphito ligands.[11] The line broadening is attributed to a statistical disorder arising from fluctuations in the positions of the coordinating ligands and to shallow potential surfaces along the Pt–Pt normal coordinates. The present observation of a single Raman band for Pt1–Pt2 and Pt1′–Pt2′ stretching is consistent with delocalization of the unpaired electron (i.e., [Pt$^{2.25}$]$_4$). A localized electron hole (i.e., Pt^{III}[Pt^{III}]$_3$) is expected to exhibit a splitting in ν(Pt1–Pt2) of $\sim$20 cm^{-1} if the hopping frequency is slower than 10^{-12} s. When **1** was prepared by using ClO$_4$$^-$ in place of NO$_3$$^-$ anions, we observed low-energy shoulders for ν(Pt2–Pt2′) and ν(Pt1–Pt2). This reproducible observation is attributed to weak coordination of the ClO$_4$$^-$ anions and not to the onset of a localized electron hole.
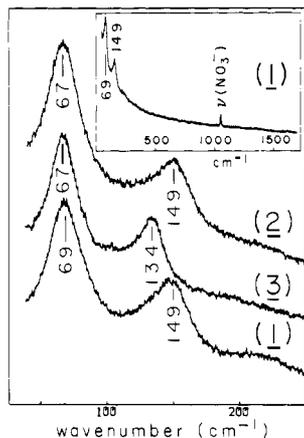
Figure 1. Resonance Raman spectra of **1**, **2**, and **3** at ~0 °C and 6764-Å laser excitation. **1** was 12 mM Pt, prepared from *cis*-diammineplatinum α-pyridone blue in 0.05 M HNO₃. **2** was 12 mM Pt, prepared from *cis*-diammineplatinum 1-methyluracil blue in H₂O. **3** was 12 mM Pt, prepared from (ethylenediamine)platinum α-pyridone blue in 0.10 M HNO₃. Insert: Resonance Raman spectrum (40–1700 cm⁻¹) of **1** at ~0 °C and 6764-Å laser excitation. **1** was 12 mM Pt, prepared from *cis*-diammineplatinum α-pyridone blue in 0.05 M HNO₃ and 0.24 M NaNO₃.

Table I. Comparison of the Optical Transitions, Pt–Pt Vibrational Frequencies, and Pt–Pt Distances of Three Pt₄⁹⁺ Cations

compd	ν(Pt–Pt),[a] cm⁻¹	optical bands,[b] nm	Pt–Pt dist,[c] Å	ref
1	149, 69	480, 680	2.774, 2.877, 2.774	4, 14, 20
2	149, 67	480, 740	2.793, 2.865, 2.810	5, 2c
3	133, 67	532, 745	2.830, 2.906, 2.830	6

[a] This work. [b] The extinction coefficients are roughly 250 and 8000 M⁻¹ cm⁻¹, respectively.[2c] [c] The second entry is the Pt2–Pt2′ distance.

ν(Pt2–Pt2′) = 84 cm⁻¹ and ν(Pt1–Pt2) = 164 cm⁻¹ and Pt1–Pt2 = 2.704 Å and Pt2–Pt2′ = 2.710 Å.[2b]

With 6764-Å laser excitation, the rR spectrum of **1** (see insert in Figure 1) displays *only* bands due to the Pt–Pt stretching vibrations and certifies that the intense optical absorption at 680 nm[14] is assigned to a metal–metal transition.[18] According to the SCF–Xα–SW calculation of **1**, the optical transition is given as a σ(Pt2–Pt2′) → σ* (Pt2–Pt2′) with some Pt1 → Pt2 charge-transfer character.[19] Raman depolarization ratios of one-third support a *z*-polarized electronic transition. The weak optical absorption at 480 nm in **1** is assigned to a π(Pt1–Pt2) → σ* (Pt1–Pt2) transition.[19] Absorption maximum, Pt–Pt distances, and ν(Pt–Pt) for **1**, **2**, and **3** are given in Table I and their low-frequency rR spectra are shown in Figure 1.

The Pt–Pt stretching frequencies are used as sensitive indicators to explain the variations in the absorption maxima of **1**, **2**, and **3**. Although the changes in ν(Pt2–Pt2′) are numerically small (2–3 cm⁻¹), they indicate a stronger Pt2–Pt2′ interaction in **1** relative to **2** or **3** and correlate well with the observed shifts of the intense optical absorption. The N–H···O interdimer hydrogen bonds stabilize the Pt₄⁹⁺ complexes and contribute to ν(Pt2–Pt2′). Differences in N–H···O bonding may result from the steric re-

quirements of the en ligands and electron density of the exocyclic oxygens. ν(Pt1–Pt2) indicates a weaker Pt1–Pt2 interaction in **3** relative to **1** or **2** and nicely correlates with the red shift of the weak optical transition observed for **3**. Nonbonding repulsions of en in adjacent coordination planes attenuate the Pt1–Pt2 bond strength in **3**.[22] The variations in the peak positions of the absorption bands originate from localized interactions of the coordinating ligands along the Pt₄⁹⁺ chain. The vibrational data demonstrate that the intense optical absorption is primarily sensitive to changes of the interdimer interactions and the weak optical absorption is primarily sensitive to changes of the intradimer Pt1–Pt2 interactions. These results are consistent with and provide support for the assignments of the optical transitions.

The crystallographic measurements of the Pt–Pt distances, as given in Table I, are compatible with the present discussion of **1** and **3**; however, the Pt–Pt distances of **2** are at variance with the analysis of the optical transitions and the rR data. It should not be surprising that structural changes occur in these interesting tetranuclear platinum complexes upon dissolution because of the feeble Pt2–Pt2′ interactions. Solid-state absorption data of **2** and **3** have not been reported to our knowledge, while differences in **1** have been observed.[19,20] Since the rR and absorption data were obtained under the same solution conditions, and present analysis is not obfuscated by this lacuna.

(22) For example, the Pt₂ⁱⁱⁱ dimer, [Pt₂(en)₂(C₅H₅NO)₂(NO₂)(NO₃)]·0.5H₂O, has a Pt–Pt bond distance of 2.64 Å (see: O'Halloran, T. V.; Roberts, M. M.; Lippard, S. J. *Inorg. Chem.* **1986**, *25*, 957) and ν(Pt–Pt) = 164 cm⁻¹.

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Reactions between Metal Carbonyl Anions and Cations: Rapid Two-Electron Transfer Followed by One-Electron Back Transfer
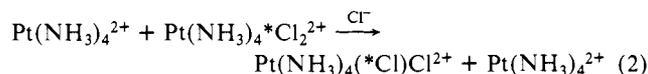
Yueqian Zhen and Jim D. Atwood*

*Department of Chemistry, University at Buffalo
State University of New York
Buffalo, New York 14214*

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Definitive examples of single-event, two-electron transfer are relatively rare. Examples of oxide transfer

$$\text{NO}_2^- + \text{OCl}^- \rightarrow \text{NO}_3^- + \text{Cl}^- \qquad (1)$$
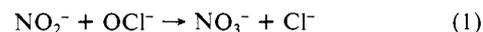
and a few examples of transition-metal complexes

$$\text{Pt(NH}_3)_4^{2+} + \text{Pt(NH}_3)_4{}^*\text{Cl}_2{}^{2+} \xrightarrow{\text{Cl}^-}$$
$$\text{Pt(NH}_3)_4(^*\text{Cl})\text{Cl}^{2+} + \text{Pt(NH}_3)_4{}^{2+} \qquad (2)$$

have been reported as two-electron transfers.[1–3] We now report, as part of our continuing study of electron-transfer reactions between organometallic complexes,[4] that reaction of Re(CO)₅⁻ with Mn(CO)₆⁺ proceeds by a rapid two-electron, one-carbonyl transfer and then a slower one-electron back transfer to the binuclear products. Self-exchange between M(CO)₅⁻ and M(CO)₆⁺ (M = Mn, Re) in acetonitrile occurs by the same steps.

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