$K_4[Pt_2(pop)_4]$ we assign the intense low-energy absorption band in this higher oligomer to a $\sigma(6p_z) \leftarrow \sigma^*(5d_{z^2})$ transition.[3,13] Excitation of aqueous 1 M HCl solutions of the complex at 360[14] and 580 nm results in an intense red luminescence at 650 nm (Figure 1). The overlap of the luminescence and low-energy absorption band and the short lifetime of the luminescence ($\tau < 0.5$ μs) indicate that the luminescence is a fluorescence.

From these data it is apparent that the product is a higher homologue of the compound $K_4[Pt_2(pop)_4]$. The pyrophosphito ligand pop is a condensation product from the reaction between two phosphorous acid molecules. Further self-condensation of $K_4[Pt_2(pop)_4]$ or condensation of $K_4[Pt_2(pop)_4]$ and phosphorous acid will lead to platinum complexes with a tetrametallic $[(HO)(O)POP(O)OP(O)OP(O)(OH)]^{4-}$ (popopop) or a trimetallic $[(HO)(O)POP(O)OP(O)(OH)]^{3-}$ (popop) chain. Laser excitation at 4880 Å of a methanol solution of the complex gives a Raman signal (ν_{PtPt}) at 85 cm^{-1}. The far-infrared spectrum (Vaseline mull) shows a band at 147 cm^{-1}. In contrast to the weak broad bands in the far-infrared spectrum of $K_4[Pt_2(pop)_4]\cdot 2H_2O$, the 147-cm^{-1} signal is by far the most intense transition below 400 cm^{-1}, typical of multimetallic complexes. With the Pt–Pt Raman stretch at 116 cm^{-1} in $K_4[Pt(pop)_4]\cdot 2H_2O$ as a reference for analyzing the data, a simple point model for a linear platinum trimer predicts one Raman-active (with frequency $116 \times (^1/_2)^{1/2} = 82$ cm^{-1}) and one infrared-active (with frequency $116 \times (^3/_2)^{1/2} = 142$ cm^{-1}) Pt–Pt stretch.[15] These results accord well with the observed frequencies and also suggest comparable Pt–Pt bond strength with the complex $K_4[Pt_2(pop)_4]$. Although additional Pt–Pt stretches are anticipated with oligomers of longer chain length,[16] the present observations do not preclude such structures.

The synthesis of oligomeric metal complexes derived from condensation reactions of phosphorous acid is under active investigation. In particular, efforts are under way to determine the precise state of aggregation of these multimetallic complexes.

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Registry No. $K_4[Pt_2(pop)_4]$, 80011-26-3; $K_2[PtCl_4]$, 10025-99-7; phosphorous acid, 10294-56-1.

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(13) A molecular orbital diagram appropriate for these oligomeric platinum(II) complexes is given in ref 12.

(14) Impure samples excited at 360 nm display a green luminescence characteristic of $K_4[Pt_2(pop)_4]$.

(15) Stein, P.; Dickson, M. K.; Roundhill, D. M., manuscript in preparation.

(16) Raman frequencies above 150 cm^{-1} are obscured by an intense fluorescent background.

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The MIME Effect: Absence of Normal Modes Corresponding to Vibronic Spacings

Sir:

Electronic emission and absorption spectra of large molecules at low temperatures frequently contain vibrational structure. When the vibrational structure exhibits a regular energy spacing, it is interpreted in terms of a single normal mode.[1] The vibronic structure, regularly spaced at 550 cm^{-1} in the luminescence spectrum of $W(CO)_5py$ (py = pyridine) shown in Figure 1, would thus be associated with a ground-state normal mode having a frequency of 550 cm^{-1}. Surprisingly, there are no totally symmetric IR or Raman bands at or near 550 cm^{-1}. We report here the first detailed observations and theoretical explanation for the "missing mode effect" or MIME. We show that absence of ground-state normal vibrational modes corresponding to an observed spacing in electronic emission spectra can occur under a wide variety of conditions.

Luminescence spectra of $W(CO)_5py$ at about 0.2-nm resolution were obtained at 3 K (single crystal, excited at 390 nm), at 10 K (single crystal, excited at 350 nm with an argon ion laser), and at 77 K in a 2-MeTHF glass.[2] In all cases a progression at 550 ± 10 cm^{-1} was observed.[2d] Infrared spectra of a Nujol mull were obtained with a Nicolet FT-IR and 30-min collection times. No totally symmetric absorptions were observed between 432 and 599 cm^{-1}. Bands that are important in the subsequent discussion were observed at 432 cm^{-1} (ν(M–C), A_1) and 599 cm^{-1} (δ(MCO), A_1).[3] Raman spectra were obtained from the solid by using 514.5-nm excitation. No Raman scattering bands were observed between 463 and 607 cm^{-1}. Raman bands corresponding to the IR bands given above were observed at 434 and 607 cm^{-1}, respectively.

Impurity luminescence leading to the observed 550-cm^{-1} progression can be ruled out for three reasons. First, spectra obtained from independent preparations purified by different means did not vary from sample to sample. Second, the luminescence from the material in a 2-MeTHF glass at 77 K occurred at the same energy and contained the same vibronic spacings as that obtained from single crystals. Finally, the 10 K absorption spectrum of a single crystal contained the same E_{00} band and a similar vibronic intensity distribution compared to those in the emission spectra. These results suggest that the electronic features do not arise from crystal defects or trace impurities.

The appearance of a 550-cm^{-1} MIME frequency generated by displacements in the 432- and 599-cm^{-1} modes can be understood from the time-dependent picture of electronic transitions.[4] This picture is equivalent to the usual Franck–Condon analysis. For an emitting molecule starting in the vibrational state ϕ, the spectrum is obtained from

$$\epsilon(\omega) = K\omega^3 \int_{-\infty}^{\infty} e^{i\omega t-\Gamma^2 t^2} \langle \phi | \phi(t) \rangle \, dt \qquad (1)$$

where K is a constant, Γ is a damping factor, and $\phi(t)$ is the

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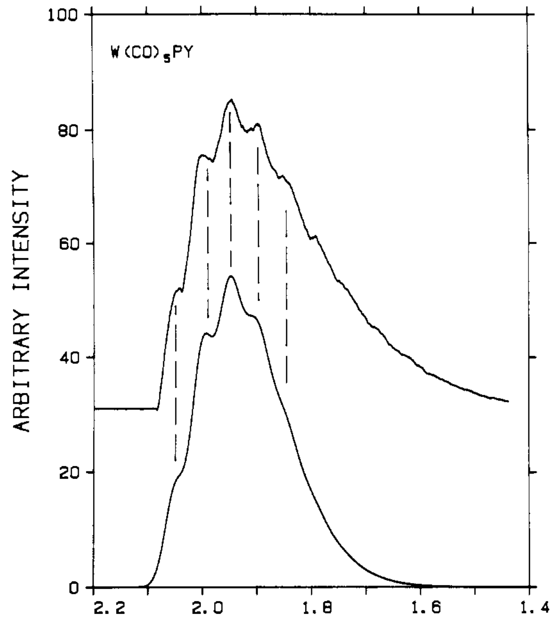

Figure 1. Top: Experimental emission spectrum of W(CO)$_5$py at 10 K. Bottom: Calculated spectrum.

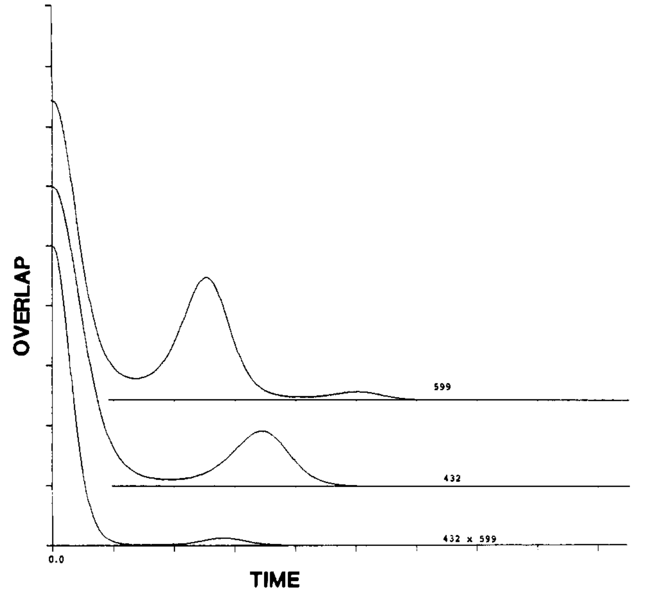

Figure 2. Top: Overlap $\langle\phi_{599}|\phi_{599}(t)\rangle e^{-\Gamma^2 t^2/2}$ vs. t. Middle: $\langle\phi_{432}|\phi_{432}(t)\rangle e^{-\Gamma^2 t^2/2}$ vs. t. Bottom: Product $\langle\phi|\phi(t)\rangle$ (see eq 2) of the above two overlaps. The Fourier transform gives the spectrum in the frequency domain shown in Figure 1 containing the 550-cm^{-1} MIME frequency.

time-dependent wave packet (with $\phi(0) = \phi$) evolving on the lower, multimode potential surface. Under the assumption of harmonic modes displaced by δ but otherwise the same in both electronic states, the overlap $\langle\phi|\phi(t)\rangle$ factors into two overlaps, one for each mode:

$$\langle\phi|\phi(t)\rangle = \langle\phi_{432}|\phi_{432}(t)\rangle\langle\phi_{599}|\phi_{599}(t)\rangle \qquad (2)$$

The evolution of these overlaps is shown in Figure 2. In each case, an initial decay is followed by a recurrence peaked at $t' = 2\pi/\omega'$, where ω' is the frequency of the mode. The occurrence is caused by the return of the moving-wave packet to its starting position. The product of the two overlaps, shown in Figure 2, occurs at $t = 0$ and $t \simeq \pm 2\pi/\omega_M$, where ω_M is the MIME 550-cm^{-1} frequency. The Fourier transform gives a regular 550 ± 7 cm^{-1} spacing in the frequency domain.

The spectrum calculated with $\delta_{432} = 1.82$, $\delta_{599} = 1.55$, and $\Gamma = 130$ cm^{-1}, shown in Figure 1, gives an excellent fit.[5] An excellent fit can also be obtained by using three of the observed totally symmetric normal-mode frequencies.[6] By changing the displacements, it is possible to tune the MIME frequency by more than 100 cm^{-1} in this case.

The MIME effect, although previously unrecognized, is not uncommon.[7] The main requirements for the MIME effect are (1) at least two displaced modes and (2) vibronic resolution on the order of that in Figure 1 caused by the damping.

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Registry No. W(CO)$_5$(py), 14586-49-3.

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(5) For convenience we transform to dimensionless normal coordinates:

$$\delta_k = \left(\frac{m_k\omega_k}{\hbar}\right)^{1/2}\Delta_k$$

The Gaussian damping Γ, due to relaxation into other modes, the "bath", etc., causes the magnitude of the recurring overlap to decrease with time as shown in Figure 2.

(6) The three frequencies used were 408 cm^{-1} (ν(M–C), A$_1$), 432 cm^{-1} (ν(M–C), A$_1$), and 599 (δ(MCO), A$_1$) with $\delta_{408} = 1.2$, $\delta_{432} = 1.1$, $\delta_{599} = 1.8$, $\Gamma = 120.0$.

(7) (a) Yersin, H.; Otto, H.; Zink, J. I.; Gliemann, G. *J. Am. Chem. Soc.* **1980**, *102*, 951. An observed vibronic spacing of 304 cm^{-1} in K$_2$PtCl$_4$ is not the expected 329-cm^{-1} (ν(M–Cl), A$_{1g}$) normal mode. The observed vibronic spacing of 395 cm^{-1} in K$_3$[Co(CN)$_6$] is not the expected 408-cm^{-1} (ν(M–CN), A$_{1g}$) normal mode. (b) Eyring, G.; Schmidtler, H. H. *Ber. Bunsenges. Phys. Chem.* **1981**, *85*, 597. An observed 455-cm^{-1} progression in [Rh(NH$_3$)$_6$]Cl$_3$ cannot be assigned to a vibrational mode of the molecule.

Preparation and Structure of Ditungsten Tetrabenzoate Bis(tetrahydrofuranate)

Sir:

We wish to report here the relatively simple and convenient preparation, in high yield and high purity, of a quadruply bonded ditungsten tetracarboxylate compound, W$_2$(O$_2$CC$_6$H$_5$)$_4$(THF)$_2$. We also describe the molecular structure, accurately determined by X-ray crystallography.

The history of attempts to make stable compounds containing W$\overset{4}{-}$W (quadruple) bonds covers a period of more than 20 years.[1] It records many failures and frustrations and relatively few successes; most of the latter are recent and in several cases would have to be considered only qualified successes. Thus, in 1977 compounds containing the [W$_2$(CH$_3$)$_8$]$^{4-}$ and [W$_2$Cl$_n$(CH$_3$)$_{8-n}$]$^{4-}$ ions were characterized:[2] these were the first authenticated compounds containing W$\overset{4}{-}$W bonds, but they are extraordinarily unstable, both chemically and thermally. The first stable, useful compound was W$_2$(mhp)$_4$ (mhp = 2-oxy-6-methylpyridine), reported[3] in 1978, and then in 1980 stable compounds of the class

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