purity of $UCl_3(THF)_x$ reagents generated by various procedures. We have observed that the $UCl_4 \cdot 15$-crown-5 adduct is very soluble in THF, probably owing to a ready dissociation of the crown ether, while UCl_3(15-crown-5) is totally insoluble. This difference allows for direct measurement of residual U(IV) without interference by the U(III) generated. Also the color of the UCl_3(15-crown-5) varies significantly with minor impurities and provides an additional qualitative measure of the purity of the $UCl_3(THF)_x$.

Studies are currently continuing on the crown ether derivatives of trivalent uranium and the chemistry of $UCl_3(THF)_x$ as a synthetic reagent for nonaqueous coordination chemistry as well as organometallic chemistry of uranium(III).

Acknowledgment. This work was performed under the auspices of the U.S. Department of Energy.

Registry No. UCl_4, 10026-10-5; Na_2Cl_2, 2881-62-1; UCl_3(15-crown-5), 71934-08-2; UCl_3(benzo-15-crown-5), 82583-23-1.

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Synthesis and Spectroscopic Properties of a New Oligomeric Condensed Phosphite Platinum(II) Complex

Sir:

The synthesis and spectroscopy of luminescent multimetallic transition-metal compounds have become a field of considerable interest. Among the compounds being studied is the bimetallic complex $K_4[Pt_2(pop)_4] \cdot 2H_2O$[1,2] formed by heating potassium tetrachloroplatinate(II) with phosphorous acid at 100 °C. The complex has evoked interest from the viewpoint of its electronic spectroscopy[3] and its photoredox chemistry.[4] Furthermore, the unusual observation of an intense room-temperature phosphorescence from aqueous solutions of $K_4[Pt_2(pop)_4]$ has led to the development of a spectrofluorometric method for the trace-element detection of platinum.[5] Another interesting feature of the chemistry of this complex is its facility to undergo oxidative addition of halogens and methyl iodide across the dimer to yield metal-metal-bonded biplatinum(III) compounds.[6] Analogous higher order oligomers would be of interest in order to investigate the effect of extended intermetallic interactions upon the electronic structure in the region between dimeric species (molecular orbital regime) and one-dimensional systems (band theory regime).

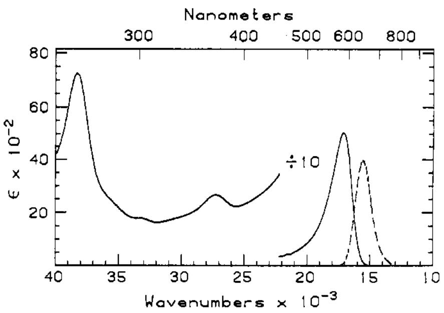

Figure 1. Room-temperature absorption (—) and luminescence (- - -) spectra of the oligomeric platinum(II) complex in aqueous 1 M HCl.

We now find that, when the synthesis of $K_4[Pt_2(pop)_4]$ is carried out at a temperature of 170 °C rather than 100 °C, the bimetallic complex is not the final product. Instead reaction proceeds beyond the bimetallic stage and a new species is formed as dark green powder.[7] This compound is soluble only in aqueous medium and decomposes within a few hours in solution to first $K_4[Pt_2(pop)_4]$ and finally $Pt\{[OP(OH)_2]_4H_2\}$. The maximum solution stability is realized when the solution is acidified to an approximate pH of 0. Blue solutions of this new complex exhibit an intense red luminescence at room temperature.

The ^{31}P NMR spectrum of this complex in acidified aqueous solution shows a broad overlapping multiplet ($\nu_{1/2} = 112$ Hz) centered at δ 62.1 and flanked by satellite peaks due to coupling with ^{195}Pt (^1J(Pt-P) = 3250 Hz). The broadness of the lines not only is due to overlapping resonances from inequivalent phosphorus nuclei but also is caused by the considerable line multiplicity from second-order effects in the spectrum. The ^{195}Pt NMR spectrum shows two poorly resolved sets of quintent resonances of unequal intensity. The sets of peaks are centered at δ -4936 (^1J(Pt-P) = 3250 Hz) and δ -4948 (^1J(Pt-P) = 3300 Hz).[8] The rate of complex decomposition precludes collection of sufficient data to resolve the ^2J(Pt-P) coupling, but the resolved ^1J(Pt-P) coupling into sets of quintets confirms that each platinum atom is tetracoordinated by phosphorus atoms. Comparison of the ^{31}P and ^{195}Pt shift positions and the magnitude of the ^1J(Pt-P) coupling shows a close similarity to those values found for the platinum(II) complex, $K_4[Pt_2(pop)_4]$, but quite a difference from those of the analogous platinum(III) compounds.[6] From these NMR spectral observations we believe the complex has a linear arrangement of divalent platinums. Magnetic susceptibility and EPR studies indicate that the platinum atoms are all diamagnetic in contrast to the mixed-valence rhodium oligomers[9] and platinum blues.[10]

The electronic absorption spectrum of the complex in aqueous 1 M HCl solution (Figure 1) shows an exceptionally intense band at 580 nm ($\epsilon = 5.0 \times 10^4$ M^{-1} cm^{-1}). No intense absorption bands were observed in the near-infrared region. The large red shift of the low-energy intense absorption band from 368 nm in $K_4[Pt_2(pop)_4]$ upon an increase of the metallic chain length has also been observed in the *solution aggregation* of rhodium isocyanide complexes.[9,11,12] By analogy with

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[1] The abbreviation pop represents $[(HO)(O)POP(O)(OH)]^{2-}$.

[2] (a) Sperline, R. P.; Dickson, M. K.; Roundhill, D. M. *J. Chem. Soc., Chem. Commun.* **1977**, 77-79. (b) Filomena Dos Remedios Pinto, M. A.; Sadler, P. J.; Neidle, S.; Sanderson, M. R.; Subbiah, A. *Ibid.* **1980**, 13-15.

[3] Fordyce, W. A.; Brummer, J. G.; Crosby, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 7061-7064.

[4] Che, C. M.; Butler, L. G.; Gray, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 7796-7797.

[5] Dickson, M. K.; Pettee, S. K.; Roundhill, D. M. *Anal. Chem.* **1981**, *53*, 2159-2160.

[6] Che, C. M.; Schaefer, W. P.; Gray, H. B.; Dickson, M. K.; Stein, P.; Roundhill, D. M. *J. Am. Chem. Soc.*, in press.

[7] In addition to this green complex a vermilion red compound is found in variable yield. This additional compound is insoluble in water and organic solvents. The nature of this compound is presently completely uncertain. These higher oligomers of $K_4[Pt_2(pop)_4]$ have also been observed by others (Gray, H. B., personal communication).

[8] ^{195}Pt NMR spectra with high-frequency shifts are referenced relative to H_2PtCl_6 at 42.8 MHz.

[9] Sigal, I. S.; Gray, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 2220-2225 and references therein.

[10] Barton, J. K.; Carawara, C.; Lippard, S. H. *J. Am. Chem. Soc.* **1979**, *101*, 7269-7277.

[11] Mann, K. R.; Gordon, J. G., II; Gray, H. B. *J. Am. Chem. Soc.* **1975**, *97*, 3553-3555.

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$K_4[Pt_2(pop)_4]$ 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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(12) Mann, K. R.; Lewis, N. S.; Williams, R. M.; Gray, H. B.; Gordon, J. G., II *Inorg. Chem.* **1978**, *17*, 828–834.

(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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(1) Herzberg, G. "Electronic Spectra of Polyatomic Molecules"; Van Nostrand: New York, 1966.

(2) (a) Dahlgren, R. M.; Zink, J. I. *Inorg. Chem.* **1977**, *16*, 3154. (b) Boxhoorn, G.; Oskam, A.; Gibson, E. P.; Norayannswarmi, R.; Rest, A. J. *Ibid.* **1981**, *20*, 783. (c) Wrighton, M. S.; Abrahamson, H. B.; Morse, D. L. *J. Am. Chem. Soc.* **1976**, *98*, 4105. (d) The 550-cm^{-1} vibronic spacings were determined by removing the broad envelope by using an FT analysis and then measuring the spacings between the remaining peak maxima.

(3) Brown, R. A.; Dobson, G. R. *Inorg. Chim. Acta* **1972**, *6*, 65.

(4) (a) Heller, E. J. *J. Chem. Phys.* **1978**, *68*, 3891. (b) Heller, E. J. *Acc. Chem. Res.*, in press. (c) Heller, E. J.; Gelbart, W. M. *J. Chem. Phys.* **1980**, *73*, 626. (d) Heller, E. J. In "Potential Energy Surface and Dynamic Calculations"; Truhlar, D. G., Ed.; Plenum Press: New York, 1981.

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