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Electron-Transfer Reactions and Luminescent Quantum Yield of the Triplet Excited State of Tetrakis[μ-diphosphito(2–)-*P*,*P*′]diplatinate(II)

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In the short period following the isolation[1] and crystal structure determination[2,3] of $Pt_2(P_2O_5H_2)_4^{4-}$ ($Pt_2(pop)_4^{4-}$), many studies have focused on its intense luminescence[4–11] and the related possibility of metal–metal bonding.[5,6,8,11–15] Although much is now known concerning the detailed nature of the lowest luminescent excited state, only a brief report[6] has appeared describing its photoredox properties. Here we report the results of excited-state electron-transfer quenching studies of $Pt_2(pop)_4^{4-}$ in methanol and also its luminescent quantum yield in aqueous solution. It is demonstrated that the triplet excited state of $Pt_2(pop)_4^{4-}$ is reduced to $Pt_2(pop)_4^{5-}$ by a series of aromatic amine quenchers and shows great promise as a photoredox catalyst.

Quenching studies were performed by standard techniques[16] and analyzed using the Stern–Volmer equation[17] to yield values of k_q, the second-order quenching rate constant. These values are presented in Table I. To correct for diffusion and encounter effects,[18] values of k_q were converted to first-order electron-transfer rate constants k_{et} by $k_{et} = [K(k_q^{-1} - k_d^{-1})]^{-1}$, where k_d is the diffusion rate constant for formation of the encounter complex with equilibrium constant K.[18]

Table I. Rate Constants for Quenching of $Pt_2(pop)_4^{4-*}$ by Aromatic Amines in Methanol Solution at ~25 °C

quencher	$E_{1/2}$, V[a]	k_q, dm³ mol⁻¹ s⁻¹ [b]	k_{et}, s⁻¹ [c]
N,*N*,*N*′,*N*′-tetramethyl-1,4-benzenediamine, 1	0.11[d]	1.2×10^{10}	6.8×10^{10}
N,*N*,*N*′,*N*′-tetramethyl-[1,1′-biphenyl]-4,4′-diamine, 2	0.36[e]	3.0×10^{9} [i]	2.5×10^{9}
N,*N*,4-trimethylbenzenamine, 3	0.71[f]	3.9×10^{7}	3.2×10^{7}
N,*N*-dimethylbenzenamine, 4	0.78[g]	1.2×10^{7}	1.0×10^{7}
N,*N*-diphenylbenzenamine, 5	0.92[h]	1.5×10^{6}	1.0×10^{6}

[a] Reduction potentials vs. SCE from cyclic voltammetric measurements in room-temperature CH_3CN solutions containing 0.1 dm³ mol⁻¹ tetraalkylammonium perchlorate. Values in CH_3OH are expected to be the same within 0.01 V (Iwa, P.; Steiner, U. E.; Vogelmann, E.; Kramer, H. E. A. *J. Phys. Chem.* 1982, *86*, 1277–1285. Horner, L.; Nickel, H. *Chem. Ber.* 1956, 1681–1690). [b] Second-order quenching rate constants obtained from slopes of Stern–Volmer plots by using $\tau_0 = 7.10 \times 10^{-6}$ s.[17] [c] First-order electron-transfer rate constant for reaction within the encounter pair. See text for explanation. [d] Luong, J. C.; Faltynek, R. A.; Wrighton, M. S. *J. Am. Chem. Soc.* 1980, *102*, 7892–7900. Values of 0.10 V[e] and 0.12 have also been reported. [e] Nocera, D. G.; Gray, H. B. *J. Am. Chem. Soc.* 1981, *103*, 7349–7350. A value of 0.43 V (ref 16 and: Zweig, A.; Maurer, A. H.; Roberts, B. G. *J. Org. Chem.* 1967, *32*, 1322–1329) has also been reported. [f] Reference 16. A value of 0.70 V[d,e] has also been reported. [g] Hino, T.; Akazawa, H.; Masuhara, H.; Mataga, N. *J. Phys. Chem.* 1976, *80*, 33–37. Luong, J. C.; Nadjo, L.; Wrighton, M. S. *J. Am. Chem. Soc.* 1978, *100*, 5790–5795. Values of 0.74 V (Jones, P. R.; Drews, M. J.; Johnson, J. K.; Wong, P. S. *Ibid.* 1972, *94*, 4595–4599), 0.79 V (Iwa, P.; Steiner, U. E.; Vogelmann, E.; Kramer, H. E. A. *J. Phys. Chem.* 1982, *86*, 1277–1285), 0.80 V,[16] and 0.81 V[e] have also been reported. The large discrepancy in these values can be partly attributed to the irreversibility of the oxidation using cyclic voltammetry.[16] [h] Debrodt, H.; Heusler, K. E. *Z. Phys. Chem.* (*Weisbaden*) 1981, *125*, 35–48. Corrected for a reference electrode difference of 0.32 V (Larson, R. C.; Iwamoto, R. T.; Adams, R. N. *Anal. Chim. Acta.* 1961, *25*, 371–374); Seo, E. T.; Nelson, R. F.; Fritsch, J. M.; Marcoux, L. S.; Leedy, D. W.; Adams, R. N. *J. Am. Chem. Soc.* 1966, *88*, 3498–3503. Values of 0.95 V (Park, S. M.; Bard, A. J. *Ibid.* 1975, *97*, 2978–2985), 1.00 V (Creason, S. C.; Wheeler, J.; Nelson, R. F. *J. Org. Chem.* 1972, *37*, 4440–4446), and 1.06[16] have also been reported. [i] For solubility reasons, 2 was first dissolved in a small amount of acetone and then added to methanol.

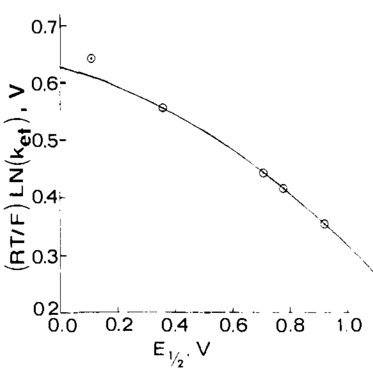

Figure 1. Plot of (RT/F) ln k_{et} vs. $E_{1/2}$ for the quenching of $Pt_2(pop)_4^{4-*}$ by a series of aromatic amines in CH_3OH at ≃25 °C. The solid line corresponds to the best fit of the data to eq 1 assuming $\nu_{et} = 10^{11}$ s⁻¹. See ref 20 for details.

The systematic variation of k_{et} with quencher $E_{1/2}$ values and the high and nearly constant quencher triplet energies[19] supports

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(17) Blazani, V.; Moggi, L.; Manfrin, M. F.; Bolletta, F.; Laurance, G. S. *Coord. Chem. Rev.* **1975**, *15*, 321–433. A value of 7.10 μs for the luminescent lifetime (deaerated CH_3OH, 25 °C) was determined from a pulsed-laser experiment.
(18) Noyes, R. M. *Prog. React. Kinet.* **1961**, *1*, 129–160. Values of k_d were calculated from the Smoluchowski equation combined with the Stokes–Einstein equation for diffusion coefficients. Radii were determined as van der Waals values (Edward, J. T. J. *Chem. Educ.* **1970**, *47*, 261–270). Values of K were calculated from the Eigen–Fuoss equation (Eigen, M. *Z. Phys. Chem.* (*Frankfurt/Main*) **1954**, *1*, 176–200. Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 5059–5061).
(19) The following triplet energies are available: **1**, 2.80 eV (Cadogan, K. D.; Albrect, A. C. *J. Phys. Chem.* **1968**, *72*, 929–944. Kuzmin, V. A.; Darmanyan, A. P.; Levin, P. P. *Chem. Phys. Lett.* **1979**, *63*, 509–514); **2**, 2.70 eV (Alkaitis, S. A.; Grätzel, M. *J. Am. Chem. Soc.* **1976**, *98*, 3549–3554); **4**, 2.99 eV (Lim, E. C.; Chakrabarti, S. K. *Chem. Phys. Lett.* **1967**, *1*, 28–31); **5**, 3.04 eV (Kuzmin, V. A.; Darmanyan, A. P.; Levin, P. P. *Ibid.* **1979**, *63*, 509–514).

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the hypothesis of electron-transfer quenching. Observation of separated redox products by flash photolysis would be unlikely in view of the Coulombic forces involved. A plot of (RT/F) ln k_{et} vs. amine $E_{1/2}$ values is shown in Figure 1.

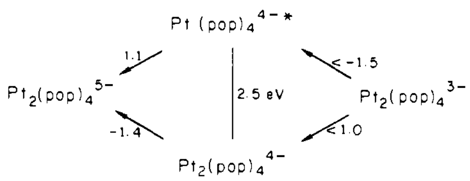
A value of 1.1 ± 0.2 V for $E°'(Pt_2(pop)_4^{4-*/5-})$ is obtained by fitting the data in Table I to the equation

$$(RT/F) \ln k_{et} = ((RT/F) \ln \nu_{et}) - (\lambda(1 + \Delta G/\lambda)^2/4) \quad (1)$$

where $\Delta G = E°'(NR_3^{+/0}) - E°'(Pt_2(pop)_4^{4-*/5-}) + w_p - w_r$ (w_p and w_r are Coulombic work terms[16]) and ν_{et} is the frequency and λ the reorganization energy for electron transfer.[20] This value is larger than the corresponding values of 0.8 V for $Ru(bpy)_3^{2+*/+}$ [16] and ≃0.5 V for $Rh_2(br)_4^{2+*/+}$ (br = 1,3-diisocyanopropane).[21] The reason for the lower k_q values for quenchers **2–4** reported here compared to those for $Ru(bpy)_3^{2+*}$ [16] is a result of the much larger value of λ for $Pt_2(pop)_4^{4-*}$ (1.4 ± 0.2 V) compared to $Ru(bpy)_3^{2+*}$ (0.5 V).[16] Since calculated values for the outer-sphere contribution to λ differ by less than 0.1 V, most of this difference can be ascribed to a larger inner-sphere reorganization energy for $Pt_2(pop)_4^{4-*}$. This is to be expected given the differing natures of the excited-state distortions for $Ru(bpy)_3^{2+}$ [22] and $Pt_2(pop)_4^{4-}$.[11]

This distortion is also expected to influence the $Pt_2(pop)_4^{4-*/5-}$ electron-transfer self-exchange rate. A maximum value of 2×10^3 dm^3 mol^{-1} s^{-1} is calculated for this rate constant using the data in Table I.[23]

An energy level diagram summarizing the excited-state redox thermodynamics in terms of $E°'$ values (V vs. SCE) can now be constructed:



where $E°'$ for $Pt_2(pop)_4^{3-/4-*}$ is from ref 9 (H_2O), and the $E°'$ values for $Pt_2(pop)_4^{4-/5-}$ and $Pt_2(pop)_4^{3-/4-}$ are calculated from the excited-state reduction potentials and E_{0-0} = 2.5 eV.[5,8,9,24] Thus, in comparison to $Ru(bpy)_3^{2+*}$, $Pt_2(pop)_4^{4-*}$ is thermodynamically both a better oxidant and reductant. This advantage is partly mitigated by the large excited-state distortion for $Pt_2(pop)_4^{4-}$, manifested in a large energy of reorganization.

Contrary to a previous report,[1] we have found $Pt_2(pop)_4^{4-}$ to be stable in acid (1.0 dm^3 mol^{-1} $HClO_4$), although decomposition to $Pt_2(pop)_4Cl_2^{4-}$ [13,15] in 1.0 dm^3 mol^{-1} HCl was observed. Thermal decomposition is rapid in basic media (pH > 10).

The quantum yield for the triplet phosphorescent state of $Pt_2(pop)_4^{4-}$ is determined to be 0.52 ± 0.07 (deoxygenated H_2O, 25 ± 3 °C).[25] This, coupled with the measured lifetime of 6.2 μs (deoxygenated H_2O, 24 °C),[4] enables values of 8.4×10^4 s^{-1} for the radiative rate constant and 7.7×10^4 s^{-1} for the nonradiative rate constant to be calculated. The long lifetime and large quantum yield both contribute to efficient excited-state reactivity.

Acknowledgment. We thank Dr. George H. Allen of the University of North Carolina at Chapel Hill for the laser lifetime measurement and Professor Allen J. Bard and Dr. Joon Kim for providing us with preliminary electrochemical results. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by a Du Pont Corp. grant to Bowdoin College, Fund 65411-5026. A generous loan of K_2PtCl_4 by the Johnson-Matthey Company is also gratefully acknowledged.

Registry No. 1, 100-22-1; **2**, 366-29-0; **3**, 99-97-8; **4**, 121-69-7; **5**, 603-34-9; $Pt_2(pop)_4^{4-}$, 80011-25-2.

(20) See eq 9, ref 16. Although in principle values of ν_{et}, λ, and ΔG can all be obtained from the data, the values for quenchers **1** and **5** were not used owing to large uncertainties in k_{et} for quencher **1** ($k_q \simeq k_d$) and $E_{1/2}$ for quencher **5** (see Table I). Therefore, it was necessary to estimate ν_{et} as 10^{11}–10^{12} s^{-1}. Values of w_p = –0.12 V and w_r = 0.00 V were used to calculate $E°'$ $(Pt_2(pop)_4^{4-*/5-})$ from ΔG.[16]

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(24) Balzani, V.; Bolletta, F.; Gandolfi, M. T.; Maestri, M. *Topics Curr. Chem.* **1978**, *75*, 1–64. Entropy contributions are assumed to be less than 0.1 eV.[5,16] Cyclic voltammetric measurements of the $Pt_2(pop)_4^{4-}$ reduction in acetonitrile indicate that it occurs at much more negative potentials than the value of –1.4 V estimated here (Bard, A. J.; Kim, J., personal communication). Since a reversible potential has not been observed, no firm conclusions can be reached.

(25) The quantum yield was determined relative to quinine sulfate in 1.0 dm^3 mol^{-1} H_2SO_4, for which Φ_{em} = 0.546 (Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991–1024). Emission spectra obtained with a Perkin-Elmer Model 654-40 fluorescence spectrophotometer were corrected for instrument response and converted to wavenumbers prior to integration (Morris, J. V.; Mahaney, M. A.; Huber, J. R. *Ibid.* **1976**, *80*, 969–974). The value reported represents the average of four determinations.

Synthesis and Structure of the First 10-P-3 Species

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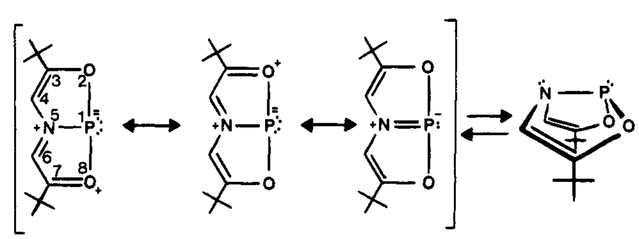
We report the synthesis and structure determination of the first 10-P-3 species, 5-aza-2,8-dioxa-3,7-di-*tert*-butyl-1-phosphabicyclo[3.3.0]octa-3,6-diene (ADPO).[1] The T-shaped phosphorus



1a **1b** **1c** **2**

ADPO

system of ADPO is the first member of a previously unknown class of compounds, a phosphorandiide.[2] ADPO can also be regarded as a phosphorus analog of the trithiapentalenes (10-S-3).

The synthesis of a compound that is free to choose between a 10- or 8-electron bonding scheme, without change in the ligation of the central atom, is of particular interest in the study of hypervalent bonding systems. For structures **1** and **2** the choice is clearly indicated by the geometry assumed by the molecule.

(1) The N-X-L system has been previously described (Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; and Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753). In the present case the N-X-L identification is necessary to distinguish between the two possible structures for the ADPO system. Care must be taken to name the most important resonance structure that is free from multiple bonds at the center being described. It should also be noted that ClF_3 assumes the same T-shaped geometry of **1** and contains the 10-Cl-3 bonding system.

(2) The name phosphorandiide is suggested by the nomenclature previously used by Granoth and Martin: Granoth, I.; Martin, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 7434.