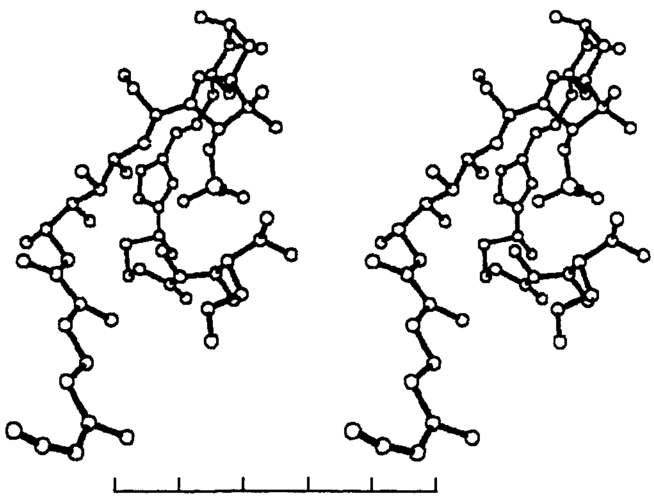
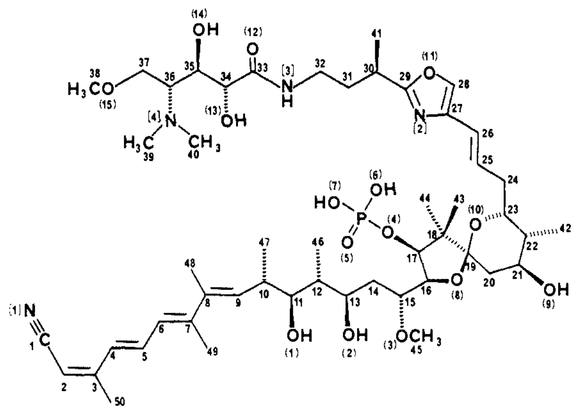


Figure 1. Computer-generated perspective drawing of calyculin A. No absolute configuration is implied.

obtained was compatible with that derived by the NMR and other spectral studies. The relative configuration and numbering scheme are shown in formula 1 and Figure 1 (10S^*,11S^*,12R^*,13R^*,15R^*,16S^*,17S^*,19S^*,21S^*,22R^*,23R^*,30R^*,34R^*,35R^*,36R^*). Calyculin A is a remarkable sponge constituent present in the animal in 0.15% of fresh weight. Its molecular structure embraces an octamethyl, polyhydroxylated C_{28} fatty acid which is linked to two γ-amino acids. The fatty acid moiety embodies a conjugated all-*E* tetraene, a β-hydroxytetrahydrofuran which is esterified by phosphoric acid and whose hetero oxygen forms a spiro ketal with a γ-hydroxytetrahydropyran. In the crystal structure we observe many intramolecular short contacts, one of which between O(1) and N(3) measures 2.99 (2) Å and forms a pseudoring. Others are with oxygen atoms of the phosphate group: O(5) and O(2) of 2.69 (2) Å, O(7) and N(4) of 2.57 (3) Å, and O(6) and N(2) of 2.81(2) Å. They contribute to a much folded molecular conformation, which may account for the resistance of the phosphate ester to either acid or enzymatic hydrolysis.



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Calyculin A is an extraordinary sponge metabolite with a rich array of functional groups. The biological role and the biosynthesis of this new natural product raise interesting questions.

Acknowledgment. Thanks are due to Professor P. J. Scheuer, University of Hawaii, for editorial comments. We are greatly indebted to K. Koseki, Japan Tobacco, Inc., for measurements of 500-MHz NMR spectra and to Dr. T. Hoshino, the Mukaishima Marine Biological Station of Hiroshima University, for identication of the sponge.

Supplementary Material Available: ^1H and ^{13}C NMR spectra and tables of additional X-ray crystallographic data (9 pages). Ordering information is given on any current masthead page.

Metal-Metal Excited-State Emission from Binuclear Platinum(III) Complexes

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Electronic emission from d^7–d^7 complexes containing metal–metal single bonds is rare; to our knowledge, the only previously reported emissions are from species with low-lying metal-to-ligand charge-transfer excited states.[1] For most d^7–d^7 compounds, the lowest electronic states involve population of the dσ* (M_2) level and are extremely short-lived,[2] precluding perceptible electronic emission.

We now report that the d^7–d^7 complexes $Pt_2(pop)_4X_2^{4-}$ (pop = $(HO_2P)_2O$; X = Cl, Br, SCN) and $Pt_2(pop)_4(py)_2^{2-}$ exhibit strong red luminescence at 77 K (Figure 1; Table I).[3] The emissions are long-lived (probably triplet → singlet) and both cation- and solvent-sensitive. Importantly, the excitation spectra for the emissions in an EtOH/MeOH glass are identical with the absorption spectra of the various complexes in the glass (Figure 2); thus we can rigorously exclude impurities (e.g., PtX_6^{2-} and PtX_4^{2-} complexes) as the source of the emission.[4]

Several of these compounds have also been examined at liquid helium temperature. One of them, $K_4[Pt_2(pop)_4Br_2]\cdot 2H_2O$, exhibits vibronic structure in its emission at this temperature (Figure 3). A long (>20 members) progression with an average vibrational interval of 125 cm^{-1} is observed. The electronic origin is not established by our data. The shortest wavelength feature we observe is at ~654 nm, but intensities are decreasing so rapidly along the progression that the true origin could well be at a still shorter wavelength.

Comparison to published[5] vibrational data for the $Pt_2(pop)_4Br_2^{4-}$ ion in room temperature aqueous solution indicates that the 125-cm^{-1} interval is energetically much too small to be a Pt–P or Pt–Br stretching frequency. The agreement with the assigned $\nu(Pt_2)$ of 134 cm^{-1} is acceptably close, considering the different conditions of the two experiments. Thus, the emissive excited state is indicated to be very strongly (because of the length of the progression) distorted along the Pt–Pt coordinate. The cation and solvent sensitivity of the emission is consistent with this type of distortion. Taken together, our data show that the emissive excited state has dσ* character, and reasonable possibilities are the triplet states derived from dσ → dσ* or dπ → dσ* excitations.[6]

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(1) Morse, D. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1976**, *98*, 3931–3934.

(2) (a) Friedman, A.; Bersohn, R. *J. Am. Chem. Soc.* **1978**, *100*, 4116–4118. (b) Rothberg, L. J.; Cooper, N. J.; Peters, K. S.; Vaida, V. *Ibid.* **1982**, *104*, 3536–3537. (c) Wrighton, M. S.; Ginley, D. S. *Ibid.* **1975**, *97*, 2065–2075.

(3) (a) $K_4[Pt_2(pop)_4X_2]$ (X = Cl, Br, SCN) and $K_2[Pt_2(pop)_4(py)_2]$ were synthesized by literature methods: Che, C.-M.; Schaefer, W. P.; Gray, H. B.; Dickson, M. K.; Stein, P. B.; Roundhill, D. M. *J. Am. Chem. Soc.* **1982**, *104*, 4253–4255. Che, C.-M.; Butler, L. G.; Grunthaner, P. J.; Gray, H. B. *Inorg. Chem.* **1985**, *24*, 4662–4665; Che, C.-M.; Lee, W. M.; Mak, T. C.; Gray, H. B. *J. Am. Chem. Soc.*, in press. The tetraphenylarsonium salts were obtained by metathesis reactions. Absorption spectra (280–700 nm) of the Ph_4As^+ salts are identical with those of the potassium salts. (b) Excitation spectra were measured with a Perkin-Elmer MPF-66 fluorescence spectrophotometer. Other emission instrumentation has been described previously (Rice, S. F.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 4571–4575). UV–vis spectra were obtained on a Hewlett-Packard 8450A diode array spectrophotometer.

(4) Impure samples of the Pt(III) complexes commonly show very weak green (λ_{max} 510–520 nm) emissions due to the $[Pt(II)]_2$ complex: Che, C.-M.; Butler, L. G.; Gray, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 7797–7797. During the course of this work we also examined samples of the mixed-valence compound $K_4[Pt_2(pop)_4Br]\cdot 3H_2O$ and could not detect any emission at 77 K.

(5) Stein, P.; Dickson, M. K.; Roundhill, D. M. *J. Am. Chem. Soc.* **1983**, *105*, 3489–3494.

(6) The intense bands near 285 and 350 nm in the absorption spectrum of $Pt_2(pop)_4Cl_2^{4-}$ (Figure 2) have been assigned to dσ → dσ* and dπ → dσ* singlet–singlet transitions[3a].

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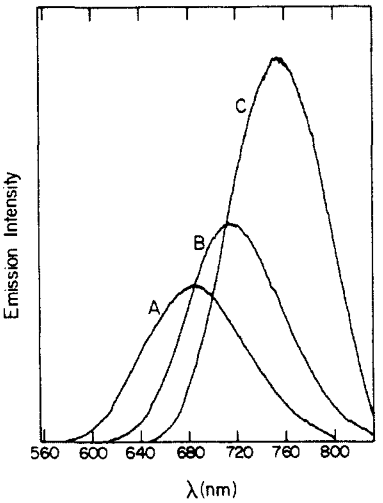

Figure 1. Corrected emission spectra at 77 K in an EtOH/MeOH glass: (A) $Pt_2(pop)_4Cl_2^{4-}$; (B) $Pt_2(pop)_4Br_2^{4-}$; (C) $Pt_2(pop)_4(SCN)_2^{4-}$.

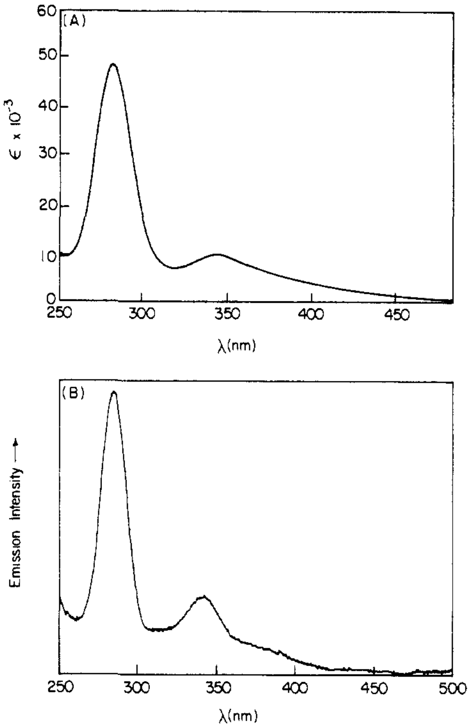

Figure 2. (A) Absorption spectrum of $Pt_2(pop)_4Cl_2^{4-}$ in aqueous solution. (B) Corrected excitation spectrum of $Pt_2(pop)_4Cl_2^{4-}$ at 77 K in an EtOH/MeOH glass.

Table I. Emission Spectral Data for $Pt_2(pop)_4X_2^{n-}$ at 77 K

	Ph_4As^+ salt: EtOH/MeOH glass		K^+ salt: solid	
X/*n*	λ_{max}, nm	τ, μs	λ_{max}, nm	τ, μs
Cl/4[a]	685	22.1	*b*	*b*
Br/4[a]	715	15.3	765	13.1
SCN/4	754	17.6	751	18.6
py/2	691	23.0	*b*	*b*

[a] Also characterized in 50% saturated LiX(aq) glass at 77 K. λ_{max} = 650 nm, τ = 13.9 μs for X = Cl; λ_{max} = 697 nm, τ = 13.3 μs for X = Br. [b] No detectable emission.

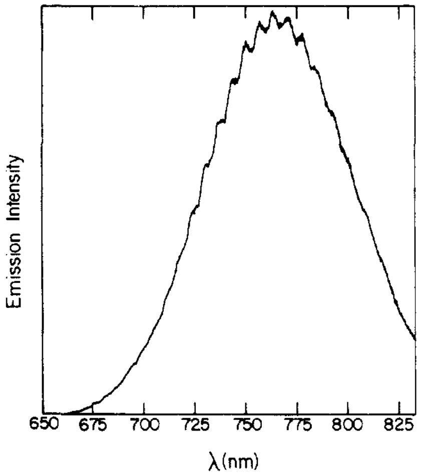

Figure 3. Corrected emission spectrum of solid $K_4[Pt_2(pop)_4Br_2]\cdot 2H_2O$ at 5 K. The vibronic spacing is 125 cm^{-1}.

Why have there been no previous examples of such emission? We think that the key in the present case is that the metal–metal bond is bridged by the four pop ligands, and metal–metal dissociation, a characteristic[2] deactivation process of d^7–d^7 excited states, is therefore prevented. The excited states of these complexes could still decay by dissociation of the axial ligands,[7] but this apparently is not an efficient process at 77 K. However, deactivation by axial-ligand dissociation may explain why our efforts to detect emission in fluid solution have thus far been unsuccessful.

Acknowledgment. We thank Mike Hopkins for assistance with the helium temperature measurements. This research was supported by National Science Foundation Grant CHE84-19828 (H.B.G.) and the Caltech President's Fund (V.M.M.).

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(7) Miskowski, V. M.; Smith, T. P.; Loehr, T. M.; Gray, H. B. *J. Am. Chem. Soc.* **1985**, *107*, 7925–7934.

Mechanisms of Hemin-Catalyzed Alkene Epoxidation. The Effect of Catalyst on the Regiochemistry of Epoxidation

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Several mechanisms have been proposed for the epoxidation of alkenes by cytochrome P-450 or relevant model hemin compounds.[1-5] Oxidants in these systems have been dioxygen or other oxygen atom donors such as peracids, iodosylbenzenes, or hypochlorite. Although all proposed mechanisms implicate the high-valent iron(IV) porphyrin cation radical $(Fe^{IV}{=}O)^+$ as the oxidizing species, they differ with regard to the nature of its reaction with alkenes. Among these are direct oxygen atom transfer (eq 1), free radical addition followed by fast ring closure (eq 2), electrophilic addition followed by fast ring closure (eq 3), reversible electrocyclic metallooxetane formation followed by

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(1) (a) Groves, J. T.; Nemo, T. E. *J. Am. Chem. Soc.* **1983**, *105*, 5786. (b) Groves, J. T.; Myers, R. S. *Ibid.* **1983**, *105*, 5791.

(2) Guengerich, F. P.; Macdonald, T. L. *Acc. Chem. Res.* **1984**, *17*, 9.

(3) (a) Ortiz de Montellano, P. R.; Kunze, K. L. *Biochemistry* **1981**, *20*, 7266. (b) Ortiz de Montellano, P. R.; Mangold, B. L. K.; Wheeler, C.; Kunze, K. L.; Reich, N. O. *J. Biol. Chem.* **1983**, *258*, 4203.

(4) Collman, J. P.; Kodadek, T.; Raybuck, S. A.; Brauman, J. I. Papazian, L. M. *J. Am. Chem. Soc.* **1985**, *107*, 4343 and references cited there.

(5) Meunier, B.; Guilmet, E.; De Carvalho, M.; Poilblanc, R. *J. Am. Chem. Soc.* **1984**, *106*, 6668.

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