producing **15b** to the virtual *exclusion* of **15a** (97:3 ratio, 82% combined). When **14** was subjected to cyclization under the same conditions (NaH, hot benzene) except in the presence of 18-crown-6, the stereoselectivity *reversed* and **15a**/**15b** was obtained in a 3.85:1 ratio (56% combined). The change in stereoselectivity can be rationalized by considering the environments of the two possible conformers (A and **B**) of the putative enolate generated from **14**. In the absence of good metal cation complexing or ligating agents, such as the reaction in benzene without crown ether, the allylic group is expected to fold over the enolate (**B**) to bring the chloride ion and sodium cation proximal in the transition state. Steric interaction between the *p*-methoxybenzyl group and the allylic halide in the alternative conformer A would accentuate the preponderance of **B**. However, in a good cation-complexing system such as the reaction in DMF or that in the presence of 18-crown-6,[10] the solvent shell surrounding the sodium would be expected to create a significant sterically compressed environment for the allylic chloride moiety in the folded conformer **B**. In this situation, conformer A would be expected to predominate and the more polar environment could facilitate solvation of the NaCl produced in the transition state. In a slightly improved procedure, reaction of **14** with NaH (10 equiv) in warm THF (5 equiv 18-crown-6) gives **15a**:**15b** in a 3-4.9:1 ratio in 64-77% combined yield.

Completion of the synthesis involved treatment of **15a** with concentrated HCl in dioxane to effect removal of the N-*t*-BOC group and olefin/cation cyclization[11] furnishing the crystalline hexacyclic indole **16** in 72% yield. Oxidation of **16** with *m*-CPBA in CH_2Cl_2/THF occurred stereospecifically, giving a single hydroxy indolenine (**17**) that was directly treated with NaOMe in MeOH furnishing the crystalline, yellow indoxyl[12] **18** in 67% overall yield from **16**. The structure of **18** was rigorously confirmed by single-crystal X-ray analysis.[13] Removal of the *p*-methoxybenzyl group proved quite difficult and was recalcitrant to the standard[14] oxidative conditions. After examining a host of reductive, oxidative, and hydrolytic conditions, it was found that treatment of **18** with excess *t*-butyllithium in THF deprotonated the benzylic position; quenching the incipient benzylic anion with oxygen effected removal of the *p*-methoxybenzyl group, affording brevianamide B (40%) that was identical by ^1H NMR, IR, TLC, and UV with an authentic sample of brevianamide B.[15] It is significant that the oxidation of **16** does not produce any of the corresponding epimeric hydroxyindolenine that would produce brevianamide A. Since brevianamide A is the major metabolite produced in nature, this raises the question whether the hypothetical biogenetic precursor **6** is oxidized enzymatically or by air autoxidation. For *both* **6** and **16**, the sterically most accessible face of the indole to autoxidation is the "brevianamide B" face.

In summary, the synthesis of brevianamide B has been achieved in 17 chemical steps and provides unambiguous evidence for the structure (**2**) tentatively proposed by Birch. The discovery of means to control the facial selectivity of the intramolecular S_N2' cyclization promises to embrace both the brevianamide/marcfortine relative stereochemistry as well as the relative stereochemistry of paraherquamide. The fundamental significance of this reaction for other applications in synthesis as well as efforts to construct **3** and **4** are in progress.

Acknowledgment. We thank the National Institutes of Health (CA43969) and the Colorado State University Agricultural Experiment Station (part of USDA SAES Western Project W-122) for financial support of this work. We also thank Professor James E. Robbers and Professor Constance M. Harris for providing samples of natural brevianamide A. The X-ray crystal structure of **18** was performed by Professor Oren Anderson, Joe Reibenspies, and Susie Miller (Colorado State University NSF-funded X-ray crystal facility). Hazel Coffman is acknowledged for growing cultures of *Penicillium brevicompactum* and providing natural samples of brevianamides A and B. James Stille is acknowledged for providing valuable technical assistance.

Supplementary Material Available: Complete spectroscopic and analytical data for all new compounds and an ORTEP stereostructure for compound **18** (7 pages). Ordering information is given on any current masthead page.

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[10] It is curious that 15-crown-5 with NaH and 18-crown-6 with KH give essentially a 1:1 ratio of **15a**:**15b**.

[11] For a related example, see: Darbre, T.; Nussbaumer, C.; Borschberg, H.-J. *Helv. Chim. Acta* **1984**, *67*, 1040.

[12] In addition to the precedent cited for the conversion of **1** → **2** via a similar oxidation/rearrangement in ref 1, see: (a) Hutchinson, A. J.; Kishi, Y. *J. Am. Chem. Soc.* **1979**, *101*, 6787. (b) Witkop, B.; Patrick, J. B. *J. Am. Chem. Soc.* **1951**, *73*, 2188.

[13] Details of the structure determination to be published elsewhere.

[14] Yoshimura, J.; Yamaura, M.; Suzuki, T.; Hashimoto, H. *Chem. Lett.* **1983**, 1001.

[15] Authentic samples of brevianamide B were obtained both from brevianamide A as described by Birch (ref 1) and from cultures of *Pencillium brevicompactum* grown in our own laboratories. The natural and synthetic materials proved to be of *opposite* absolute configuration as evidenced by the opposite signs of the respective specific rotations: natural $[\alpha]^{25}_D$ +124° (*c* 0.77, CH_2Cl_2/2.5% HCO_2H); synthetic $[\alpha]^{25}_D$ -124° (*c* 0.77, CH_2Cl_2/2.5% HCO_2H). The absolute configuration of the synthetic material is that depicted in the manuscript.

First EPR Spectroscopic Detection of Photochemically Generated Carbonyloxyl Radicals in Solution under Steady-State Conditions[1]

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The direct detection of carbonyloxyl radicals, $XCO_2^{\bullet}$, in solution has proven to be extremely difficult. There is only one report of their detection in solution by EPR spectroscopy:[3,4] Yamauchi et al.[3] used a modified spectrometer with a very fast response to obtain time-resolved EPR spectra in the absorption mode (rather than the normal, first derivative spectra) for three aroyloxyl radicals, $ArCO_2^{\bullet}$, that had been generated by 308 nm laser flash photolysis (LFP) of the corresponding diaroyl peroxides in CCl_4. We have studied the kinetic behavior of numerous aroyloxyl[7] and alkoxycarbonyloxyl,[8] $ROCO_2^{\bullet}$, radicals produced by LFP of suitable precursors in solution by monitoring absorptions that these radicals possess in the visible region of the spectrum.[9] These kinetic studies led us to hypothesize that $XCO_2^{\bullet}$ radicals which would yield destabilized $X^{\bullet}$ radicals and hence might be expected to have relatively strong $X\text{-}CO_2^{\bullet}$ bonds ought to be observable

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[3] Yamauchi, S.; Hirota, N.; Takahara, S.; Sakuragi, H.; Tokumaru, K. *J. Am. Chem. Soc.* **1985**, *107*, 5021-5022.

[4] $HO_2CCH{=}CHCO_2^{\bullet}$,[5a-d] $HO_2CC{\equiv}CCO_2^{\bullet}$,[5e] and $C_6H_5CO_2^{\bullet}$[6] radicals have been detected by EPR in crystals at temperatures of 77 K and lower.

[5] (a) Iwasaki, M.; Eda, B.; Toriyama, K. *J. Am. Chem. Soc.* **1970**, *92*, 3211-3212. (b) Toriyama, K.; Iwasaki, M.; Noda, S.; Eda, B. *Ibid.* **1971**, *93*, 6415-6421. (c) Eda, B.; Iwasaki, M. *J. Chem. Phys.* **1971**, *55*, 3442-3449. (d) Minakata, K.; Iwasaki, M. *Ibid.* **1972**, *57*, 4758-4763. (e) Muto, H.; Toriyama, K.; Iwasaki, M. *Ibid.* **1972**, *57*, 3016-3017.

[6] (a) Karch, N. J.; Koh, E. T.; Whitsel, B. L.; McBride, J. M. *J. Am. Chem. Soc.* **1975**, *97*, 6729-6743. (b) McBride, J. M.; Merrill, R. A. *Ibid.* **1980**, *102*, 1723-1725.

[7] (a) Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1987**, *109*, 897-899; (b) **1988**, *110*, 2877-2885; (c) **1988**, **110**, 2886-2893.

[8] Chateauneuf, J.; Lusztyk, J.; Maillard, B.; Ingold, K. U. *J. Am. Chem. Soc.*, in press.

[9] As first indicated by the photodecarboxylation of vinylcarbonyloxyl[5] and benzoyloxyl[6a] radicals by visible light.

Table I. EPR Spectroscopic Parameters for Some Carbonyloxyl Radicals[a]

radical	solvent	*T* (K)	*g*	hfs (Gauss)
1 *trans*-$Me_3CCH{=}CHCO_2^\bullet$	c-C_3H_6	145	2.01176(3)	H: 2.13 (3); H: 0.46 (2)
1 *trans*-$Me_3CCH{=}CHCO_2^\bullet$	$CFCl_3$	158	2.0118(1)	H: 2.10 (5); *b*
2 $Me_3CC{\equiv}CCO_2^\bullet$	$CFCl_3$	162	2.0126(1)	
$Me_3CC{\equiv}C^{13}CO_2^\bullet$	$CFCl_3$	160	2.0125(1)	^{13}C: 13.3 (1)
$Me_3CC{\equiv}^{13}CCO_2^\bullet$	$CFCl_3$	155	2.01264(5)	^{13}C: 4.92 (4)
3 $CH_3CH_2CH_2OCO_2^\bullet$	c-C_3H_6	145	2.0128(1)	

[a] Numbers in parentheses indicate the probable error in the last digit. [b] hfs by the second H was not resolved because a higher modulation amplitude was employed.

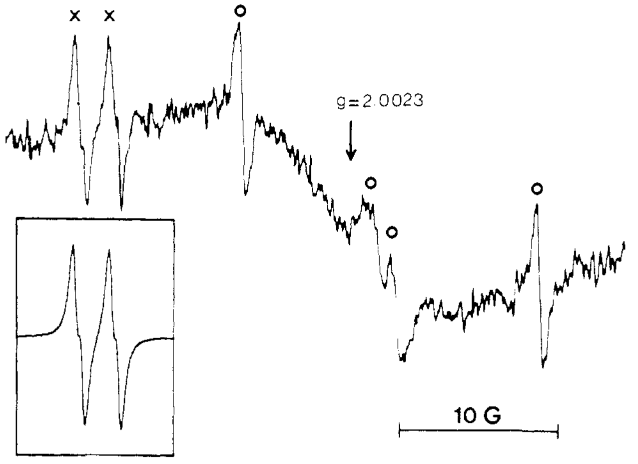

Figure 1. EPR spectrum obtained on photolysis of $(Me_3CCH{=}CHCO_2)_2$ in cyclopropane solution at 147 K, showing alkenylcarbonyloxyl radical **1** (X) and some acyl-type radicals (O). Microwave power and modulation amplitude were 10 mW and 0.125 G, respectively. The insert shows a computer simulation of the carbonyloxyl spectrum.

in solution by using standard, steady-state EPR spectroscopic techniques with an unmodified spectrometer. Such has proven to be the case.

Direct UV photolysis in the cavity of a Varian E104 EPR spectrometer with a 1000 W high pressure Hg lamp of (*trans*-$Me_3CCH{=}CHCO_2)_2$,[10] $(Me_3CC{\equiv}CCO_2)_2$,[11] and $(CH_3CH_2CH_2OCO_2)_2$[12] in cyclopropane or Freon 11 as solvents at low temperatures yielded first-derivative spectra of the corresponding alkenylcarbonyloxyl, **1**, alkynylcarbonyloxyl, **2**, and alkoxycarbonyloxyl,[13] **3**, radicals together with signals arising from secondary radical reactions[15] (see Table I and Figures 1 and 2).

The EPR spectra of the carbonyloxyl radicals, **1**, **2**, and **3**, have fairly sharp lines ($\Delta H_{pp} \sim 0.3$–0.4 G) and *g* values in the range 2.0117–2.0128. These signals are assigned to the appropriate $XCO_2^\bullet$ radical for the following reasons: (i) The *g* values are in satisfactory agreement with the available, though rather limited, literature data.[16] (ii) *trans*-$Me_3CCH{=}CHCO_2^\bullet$, **1**, shows additional hyperfine splittings (hfs) of ~2.1 and 0.4 G due to two different hydrogen atoms.[18] (iii) The $XCO_2^\bullet$ EPR spectral lines were not eliminated by molecular oxygen (which, however, did suppress the other signals arising from "secondary" radicals, apparently converting them to peroxyl radicals[19]). (iv) The $XCO_2^\bullet$ lines were suppressed by the addition of compounds such as styrene, 1,4-cyclohexadiene, and toluene that we have previously shown to be highly reactive toward aroyloxyl[7] and alkoxycarbonyloxyl[8] radicals. (v) Saturation of the $XCO_2^\bullet$ EPR signals occurred only at fairly high microwave power levels (maximum signal height at ca. 20 mW), a phenomenon that has been observed for at least some other oxygen-centered radicals.[20] (vi) Photolysis of $(Me_3CC{\equiv}C^{13}CO_2)_2$[21] gave a radical, $Me_3CC{\equiv}C^{13}CO_2^\bullet$, which had a ^{13}C hfs of 13.3 G, implying that there is only ca. 1% 2s spin density on the carbonyl carbon atom. A hfs of this magnitude is consistent with the prevailing view (based on solid-state EPR measurements[6b] and theoretical calculations[22]) that $XCO_2^\bullet$ radicals have a $^2B_2$ σ electronic ground state with the unpaired electron residing equally on the two oxygen atoms and with little spin density on the central carbon atom.[23] (vii) Photolysis of $(Me_3CC{\equiv}^{13}CCO_2)_2$[24] gave a radical, $Me_3CC{\equiv}^{13}CCO_2^\bullet$, which had a ^{13}C hfs of 4.92 G. Our two measured ^{13}C hfs may be compared with INDO calculations on $HC{\equiv}CCO_2^\bullet$ by using the

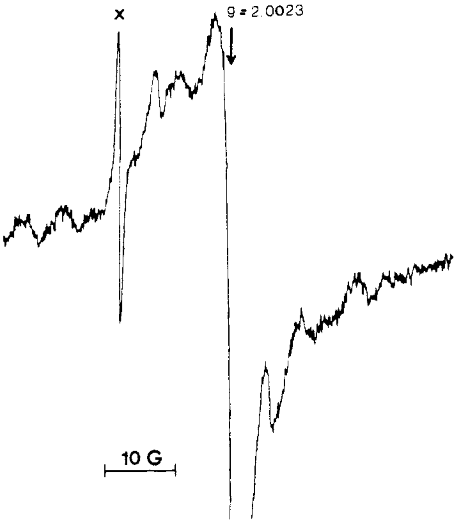

Figure 2. EPR signal of the alkynylcarbonyloxyl radical **2** (X), recorded during photolysis of $(Me_3CC{\equiv}CCO_2)_2$ in $CFCl_3$ at 162 K and 2 mW microwave power. The strong signals in the center of the spectrum are tentatively assigned to some vinyl-type radicals.[15]

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(10) Mp 68–69 °C; ^1H NMR (CCl_4, TMS int), δ (ppm) 7.04 (1 H), 5.70 (1 H), 1.15 (9 H); IR 1795, 1770 ($\nu_{C=O}$) cm^{-1}.

(11) Mp 60–63 °C; ^1H NMR (CCl_4, TMS int), δ (ppm) 1.36; IR, 2240 ($\nu_{C\equiv C}$), 1787, 1763 ($\nu_{C=O}$) cm^{-1}.

(12) From Lucidol Penwalt, used as received.

(13) In a much earlier study, Edge and Kochi[14] did not detect $ROCO_2^\bullet$ radicals upon UV irradiation of solutions of peroxydicarbonates in cyclopropane at low temperatures in the cavity of an EPR spectrometer. However, in the presence of various olefins they did obtain strong EPR spectra of $ROCO_2^\bullet$/olefin adduct radicals.

(14) Edge, D. J.; Kochi, J. K. *J. Am. Chem.* Soc. **1973**, *95*, 2635–2643.

(15) These include acyl radicals, $R\dot{C}O$ ($g \sim 2.0005$–2.0007), the signal intensities for which increase with increasing duration of photolysis. The probable origin of these and some other secondary radicals will be considered in a full paper.

(16) Isotropic *g* values calculated from crystal data: *trans*-$ZO_2CCH{=}CHCO_2^\bullet$, 2.0112 (*Z* = negative charge), 2.0119 (Z = H, D);[5a–c] *cis*-$ZO_2CCH{=}CO_2^\bullet$, 2.0127 (*Z* = negative charge), 2.0105 (Z = D);[5d] $HO_2CC{\equiv}CCO_2^\bullet$, 2.0142;[5e] $C_6H_5CO_2^\bullet$, 2.0117;[6a] $HO_2CCH_2CH_2CO_2^\bullet$, 2.009.[17] For $C_6H_5CO_2^\bullet$ and 4-$CH_3OC_6H_4CO_2^\bullet$ *g* = 2.0123 and 2.0121, respectively.[3]

(17) Box, H. C.; Freund, H. G.; Lilga, K. T.; Budzinski, E. E. *J. Phys. Chem.* **1970**, *74*, 40–52.

(18) For comparison, *cis*-$ZO_2CCH{=}CHCO_2^\bullet$ (*Z* = negative charge or H) have an isotropic H hfs of 3.9 G.[5a–c] This hfs was not analyzed for the corresponding trans radicals.[5d]

(19) As indicated by the appearance of strong, broad EPR signals with *g* ~ 2.015–2.018.

(20) E.g., peroxyl radicals, $ROO^\bullet$, and nitroxide radicals, $R_2NO^\bullet$.

(21) Synthesized via $^{13}CO_2$ carboxylation of *tert*-butylactylene, see: Bohlmann, F.; Brehm, M. *Chem. Ber.* **1979**, *112*, 1071–1073.

(22) Peyerimhoff, S. D.; Skell, P. S.; May, D. D.; Buenker, R. J. *J. Am. Chem. Soc.* **1982**, *104*, 4515–4520. Feller, D.; Huyser, E. S.; Borden, W. T.; Davidson, E. R. *Ibid.* **1983**, *105*, 1459–1466. McLean, A. D.; Lengsfield, G. H., III; Pacansky, J.; Ellinger, Y. *J.* Chem. *Phys.* **1985**, *83*, 3567–3576.

(23) For the carboxyl carbon atom McBride and co-workers'[6a] INDO calculations on $HCO_2^\bullet$ with C_{2v} geometry and in the $^2B_2$ state have yielded ^{13}C hfs of −34.5 G (standard bond lengths) and −9.3 G (optimized geometry) and on $C_6H_5CO_2^\bullet$ with C_{2v} geometry and in the $^2B_2$ state ^{13}C hfs of −42.6 G and with C_1 geometry (unequal bond lengths) and in the $^2\Sigma$ state, −14.1 G.

(24) Synthesized[21] from commercial $Me_3CC{\equiv}^{13}CH$ (MSD Isotopes).

AM1-optimized geometry which gave ^{13}C hfs of −22.2 and +16.5 G for $\mathrm{HC{\equiv}C^{13}CO_2^{\bullet}}$ and $\mathrm{HC{\equiv}^{13}CCO_2^{\bullet}}$, respectively,[23] and with an experimental value of −13.3 G measured for $\mathrm{C_6H_5{}^{13}CO_2^{\bullet}}$ in an acetyl benzoyl peroxide single crystal at 35–40 K.[26]

The peroxide precursors of **1** and **2** were also subjected to 308 nm LFP and were found to yield transient absorptions in the visible region of the spectrum, as we have found previously for aroyloxyl[7] and alkoxycarbonyloxyl[8] radicals. We assign these absorptions to the expected alkenylcarbonyloxyl and alkynylcarbonyloxyl radicals for the usual reasons, e.g., "instantaneous" (⩽4 ns) formation following LFP, lifetimes that are the same in N_2-saturated as in O_2-saturated solutions, etc.[7,8] LFP measurements[7,8] indicate that the alkenylcarbonyloxyl radical is of comparable reactivity to benzoyloxyl[7c] and that the alkynylcarbonyloxyl radical has a reactivity greater than benzoyloxyl[7c] but generally somewhat lower than alkoxycarbonyloxyl[8] radicals. For example, in CCl_4 at ambient temperatures the bimoleuclar rate constants for reactions of *trans*-$\mathrm{Me_3CCH{=}CHCO_2^{\bullet}}$, $\mathrm{C_6H_5CO_2^{\bullet}}$, $\mathrm{Me_3CC{\equiv}CCO_2^{\bullet}}$, and $\mathrm{CH_3CH_2CH_2OCO_2^{\bullet}}$ with styrene are 0.33, 0.51, 5.3, and 20 × 10^8 M^{-1} s^{-1}, respectively, and with 1,4-cyclohexadiene 1.3, 0.66, 9.2, and 9.9 × 10^8 M^{-1} s^{-1}, respectively. As before,[8] we attribute differences in the reactivities of different $\mathrm{XCO_2^{\bullet}}$ radicals to variations in the importance that polar, canonical structures (e.g., $[\mathrm{XCO_2^-}\ \mathrm{RH^{\bullet+}}]^{\ddagger}$) contribute to the stabilization of the transition state for the reaction.

The detection of carbonyloxyl radicals by EPR spectroscopy under normal experimental conditions opens a new avenue for the exploration of the chemical and spectroscopic properties of these highly reactive and industrially important species.

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[25] For $\mathrm{HCC{\equiv}CCO_2^{\bullet}}$ the AM1-optimized geometry of the carboxyl moiety is r(C–O) = 1.343 and 1.235 Å, r(C–C) = 1.423 Å, and <(O–C–O) = 116.6°. In the case of a forced C_{2v} geometry the AM1-optimization gives r(C–O) = 1.284 Å, r(C–C) = 1.422 Å, and ⟨(O–C–O) = 122.1°, and the calculated ^{13}C hfs increases to −36.8 G. We are indebted to Dr. W. Müller, Universität Essen, for carrying out these calulations.

[26] Merril, R. A. Ph.D. Thesis, Yale University, 1986; *Disser. Abstr. Int., B* **1987**, *47*, 3372. We are indebted to Dr. J. M. McBride for drawing this work to our attention.

Luminescent Exciplex Formation Involving Tetrakis(μ-diphosphito)diplatinate(II) and -thallium(I) in Aqueous Solution

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The formation of exciplexes involving singlet organic excited states is well documented.[1-3] While the properties of such exciplexes are often easily probed as a result of strong fluorescence, such is not the case for triplet exciplexes; like most other triplet organic excited states little or no luminescence is observed and only indirect measures of their properties are available.[4,5] This situation is found also for triplet exciplexes involving metalloporphyrins and various electron acceptors[6,7] and for copper (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)$_2$ and various Lewis bases.[8] However, there have been recent reports of luminescent triplet exciplex formation involving rhenium (4,7-dimethyl-1,10-phenanthroline)(CO)$_3$Cl and *N,N*-dimethylbenzeneamine in decahydronaphthalene solution[9] and ruthenium (2,2′-bipyridine)$_3{}^{2+}$ and Ag^+ in aqueous solution.[10]

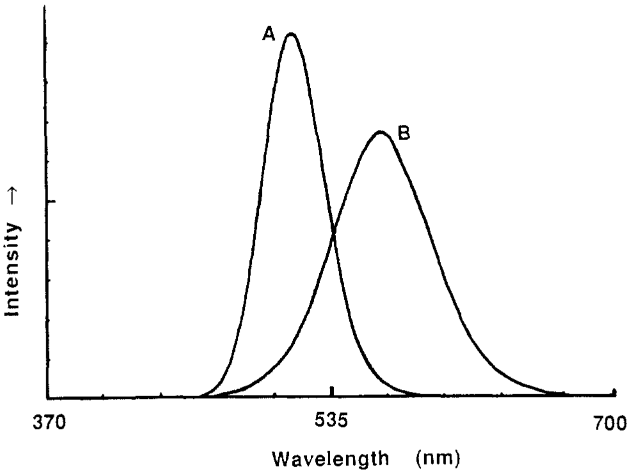

Figure 1. Corrected emission spectra of (A) 10^{-5} M $\mathrm{Pt_2(P_2O_5H_2)_4{}^{4-}}$ and (B) 10^{-5} M $\mathrm{Pt_2(P_2O_5H_2)_4{}^{4-}}$ and 10^{-3} M $TlNO_3$, both in deoxygenated water at room temperature. About 5% of the 514-nm band appears superimposed on the 565-nm band in (B). The absorption (and corrected emission) spectra for (A) and (B) are nearly identical.

Evidence is presented here for the formation of a strongly luminescent triplet exciplex involving $\mathrm{Pt_2(P_2O_5H_2)_4{}^{4-}}$ (Pt_2; singlet ground state) in its triplet excited state (Pt_2*)[11,12] and Tl^+ in aqueous solution. As suggested below we believe this to involve Pt–Pt–Tl covalent bonding. Other reports of purely inorganic luminescent exciplexes have appeared[13] but with less direct evidence than reported here. To our knowledge this is the first report of exciplex formation involving a metal–metal-bonded complex.

Figure 1 shows the effect of adding $TlNO_3$ to an aqueous solution of Pt_2 irradiated at either 368 or 453 nm. The green 514-nm phosphorescence of Pt_2* is replaced by a yellow-green luminescence centered at 565 nm (with intermediate concentrations of Tl^+ an isoluminescent point is seen at about 535 nm);[14,15] the 405-nm fluorescence[11] (produced only by 368-nm excitation and not shown on this scale) is unaffected by Tl^+. The measured lifetime (10.2 ± 0.2 μs[16]) and quantum yield (0.53 ± 0.03[17]) of

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[12] The 10^7 ratio of 514–405-nm lifetimes for Pt_2*,[11] the 3 × 10^2 ratio of 368–453-nm molar absorptivities, and the relative energies of the two absorption and two luminescence bands all support the use of singlet–triplet designations.

[13] Marcantonatos, M. D.; Deschaux, M. *Chem. Phys. Lett.* **1981**, *80*, 327–333. Deschaux, M.; Marcantonatos, M. D. *J. Inorg. Nucl. Chem.* **1981**, *43*, 2915–2917.

[14] Tl^+ luminesces in aqueous solutions but only at substantially higher energies than seen here (Sheperd, T. M. *J. Chem. Soc., Faraday Trans 2* **1979**, *75*, 644–650).

[15] As [Tl^+] is increased from 10^{-3} M to 0.2 M, the absorption (and excitation) band at 368 nm is replaced by one at 389 nm, and the 565-nm luminescence band is replaced by one at 589 nm. Owing to the absorption change, such effects are not considered further here but are currently being investigated. Note that according to ref 2 (p 140), "The 'instability' of the ground state complex is a somewhat arbitrary feature of the excimer and exciplex definition. The essential idea is that the ground state ... collision complexes are *unstable*, low-structured species, *not* that they lack a measurable absorption spectrum." See also ref 25.

[16] Lifetimes of deoxygenated solutions were determined with a Laser Science VSL-337 pulsed nitrogen laser used to pump a DCM-1 dye laser with PPO-365 dye.

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