SSCE) which readily reduce alkylated pyridinium groups.[7] Accordingly, when R is changed to N-bound pyridine (py) or 4-phenylpyridine (4-Ph-py), luminescence from both excited singlet and triplet states is severely quenched. On the basis of an unquenched singlet lifetime of 100 ps, the steady-state emission quantum yields of the two quenched complexes indicate singlet lifetimes of less than 2 ps. If electron transfer is the sole source of this nonradiative singlet decay, then the charge-separation rate constants are greater than 5×10^{11} s^{-1}.

Picosecond transient absorption spectroscopy provided additional insight into the excited-state decay kinetics. Excitation of the py and 4-Ph-py complexes with 532-nm,[8] 30-ps laser pulses generates transient species that decay exponentially with lifetimes of 130 and 54 ps, respectively. The difference spectrum of the py transient (circles, Figure 1b) is consistent with that of the electrochemically generated species $[Ir(\mu\text{-pz}')(CO)(PPh_3)]_2^+$ but also closely resembles the spectra of the singlet and triplet Ir_2 excited states (Figure 1a). The *N*-alkyl-py$^\bullet$ radical has no strong absorption bands in the 310-700-nm spectral region[9] which might confirm an assignment for the py transient. The difference spectrum of the 4-Ph-py transient (triangles, Figure 1b) exhibits, in addition to the bleach of the 460-nm ground-state absorption band, a strong feature maximizing near 350 nm and a weaker band at about 525 nm. This difference spectrum, which is quite distinct from the singlet and triplet difference spectra, is characteristic of the *N*-alkyl-4-Ph-py$^\bullet$ radical[10] and demonstrates that electron transfer occurs on a time scale comparable to or shorter than the duration of the laser pulse. By analogy with the 4-Ph-py complex, the py transient is most likely a charge-separated species. The measured 7.7×10^9 and 1.9×10^{10} s^{-1} rate constants, therefore, correspond to the electron-hole recombination rates in the py and 4-Ph-py complexes, respectively.

The rates of photoinduced electron transfer in the py and 4-Ph-py complexes approach 10^{12} s^{-1} which, depending upon the choice of preexponential factor, is within about a factor of ten of the fastest possible electron-transfer rates. The time scale of these virtually barrierless electron transfers ($E_a < 0.1$ eV[12]) is nearing that of intramolecular rotations[13] and solvent relaxation[14] such that the dynamics of these processes might be reflected in the charge-separation kinetics. The thermal back-reactions are about two orders of magnitude slower than the photoinduced electron transfers. These observations are especially noteworthy in view of the fact that the free energy changes for the back-reactions exceed those of the photoinduced reactions by as much as 0.5 eV. The relative rates of the charge-separation and recombination reactions in these systems reflect an important interplay among driving force, reorganization energy (λ), and donor-acceptor separation (r). The Marcus theory predicts that the reaction with a free-energy change *closer* to the reorganization energy will be the faster process.[1a] Brunschwig et al.[15] have noted that while the donor-acceptor electronic coupling (κ) *decreases* with r, the outer-sphere contribution to λ *increases* with r. Hence, the *ratio* of forward to back-reaction rates will be a function of donor-acceptor separation because of the distance dependences of κ, λ, and $\Delta G°$.[16]

The results described above demonstrate that the Ir_2-based donor-acceptor system is well-adapted to detailed studies of intramolecular electron-transfer reactions. Driving forces can be adjusted over a wide range of potentials;[7] modifications of the donor-acceptor linkage can be used to examine the importance of distance and orientation on electron-transfer rates, and the effects of rate-limiting nuclear motions can be probed in studies of the extremely rapid charge-separation reactions.

Acknowledgment. We thank Drs. Norman Sutin, Carol Creutz, and Dan Dubois for helpful discussions and suggestions during the course of this work. Research performed at Brookhaven National Laboratory was carried out under contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences. Research at the California Institute of Technology was supported by National Science Foundation Grant CHE84-19828.

(7) Marshall, J. L.; Stobart, S. R.; Gray, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 3027-3029.

(8) The two model complexes and the py complex exhibit virtually identical transient absorption behavior with 355- and 532-nm excitation. The 4-Ph-py group luminesces upon 355-nm laser excitation so 532-nm excitation was necessary for measurement of the electron-transfer kinetics.

(9) Kosower, E. D.; Land, E. J.; Swallow, A. J. *J. Am. Chem. Soc.* **1972**, *94*, 986-987.

(10) The spectrum of the *N*-alkyl-4-Ph-py$^\bullet$ radical should resemble that of the protonated 4,4'-bipyridine radical which has a strong, sharp band at 385 nm (ϵ = 37 000 M^{-1} cm^{-1}) and a weaker broad band at 570 nm (ϵ = 13 000 M^{-1} cm^{-1}).[5b,11]

(11) Creutz, C. *Comments Inorg. Chem.* **1982**, *1*, 293-311.

(12) Estimate based on the observed rate constants and a frequency factor of 10^{13} s^{-1}. The rate constants will require a statistical correction factor to account for the presence of two electron acceptors.

(13) (a) Brown, M. S.; Grant, D. M.; Horton, W. J.; Mayne, C. L.; Evans, G. T. *J. Am. Chem. Soc.* **1985**, *107*, 6698-6707. (b) Lyerla, J. R.; McIntyre, H. M.; Torchia, D. A. *Macromolecules* **1974**, *7*, 11-14.

(14) (a) Hynes, J. T. *J. Phys. Chem.* **1986**, *90*, 3701-3706. (b) Sumi, H.; Marcus, R. A. *J. Chem. Phys.* **1986**, *84*, 4894-4914.

(15) Brunschwig, B. S.; Ehrenson, S.; Sutin, N. *J. Phys. Chem.* **1986**, *90*, 3657-3668.

(16) Brunschwig, B. S.; Ehrenson, S.; Sutin, N. *J. Am. Chem. Soc.* **1984**, *106*, 6858-6859.

Factor S_1, a Natural Corphin from *Propionibacterium shermanii*

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Received June 30, 1987

Recent studies[1,2] on the methylation sequence of vitamin B_{12} biosynthesis have revealed that eight methyl groups from *S*-adenosylmethionine (SAM) are inserted into uro'gen III (**1**) in the order $C_2 > C_7 > C_{20} > C_{17} > C_{12} > C_1 > C_5 \approx C_{15}$ on the way to cobyrinic acid (**5**) and that factors I (**2**), II (**3**), and III (**4**) constitute the known intermediates *post* uro'gen III,[3] containing one, two, and three SAM-derived methyl groups, respectively (Scheme I).

On the basis of the sequential methylation data, our search for tetramethylated species by $^3H/^{14}C$ double labeling in cobalt-*deficient* cell free extracts and whole cells of *Propionibacterium shermanii* in the presence of δ-aminolevulinic acid (ALA) and SAM has uncovered four new isomeric zinc complexes, factors S_1-S_4[4] ($C_{44}H_{51}O_{16}N_4ZnCl$), which were purified by extensive TLC

(1) Scott, A. I.; Mackenzie, N. E.; Santander, P. J.; Fagerness, P. E.; Müller; G.; Schneider, E.; Sedlmeier, R.; Wörner, G. *Bioorg. Chem.* **1984**, *12*, 356.

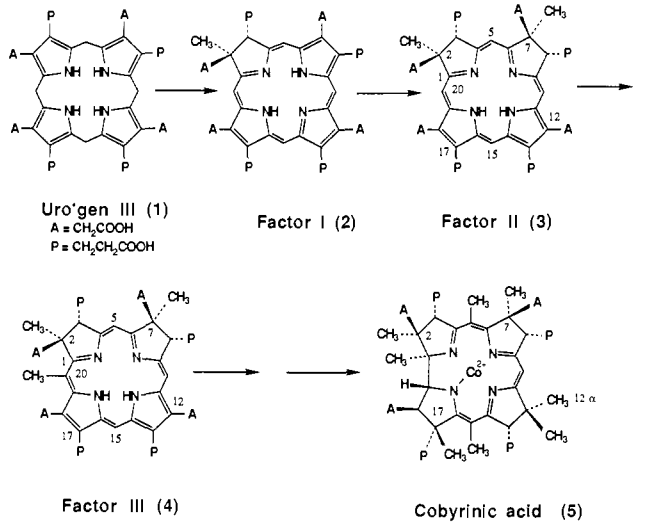
(2) Uzar, H.; Battersby, A. R. *J. Chem. Soc., Chem. Commun.* **1982**, 1204; **1985**, 585.

(3) Review: Scott, A. I. *Pure Appl. Chem.* **1986**, *58*, 753. The reduced forms of factors I-III are probably the true biochemical intermediates.

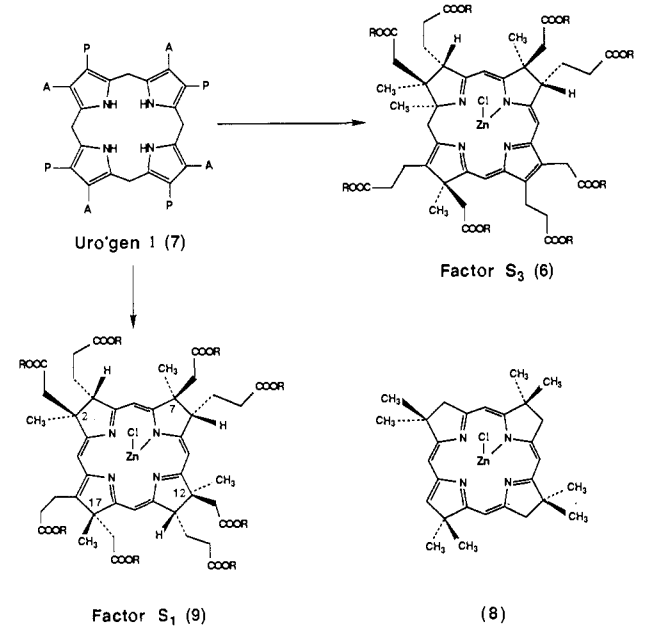
(4) Müller, G.; Schmiedl, J.; Schneider, E.; Sedlmeier, R.; Wörner, G.; Scott, A. I.; Williams, H. J.; Santander, P. J.; Stolowich, N. J.; Fagerness, P. E.; Mackenzie, N. E.; Kriemler, H.-P. *J. Am. Chem. Soc.* **1986**, *108*, 7875; Schmiedl, J. Dissertation, University of Stuttgart, 1987.

0002-7863/87/1509-6902$01.50/0

Scheme I



Scheme II



of their octamethyl esters. The structure **6** of the most abundant isomer, factor S_3, contains the unique corphin-like structure formed by methylation of the uro'gen I template at one α- and three β-positions.[4] In this communication we present evidence for the structure of a second isomer, factor S_1, also derived from uro'gen I (**7**) which is the first example of a true corphin to be found in nature (Scheme II).

FD and high resolution FAB-MS confirmed the formula of the octamethyl ester of factor S_1 as $C_{52}H_{67}O_{16}N_4ZnCl$. Comparison of the UV–vis spectrum of S_1[5] with that of the synthetic zinc corphinato chloride (**8**)[6] reveals close correspondence. With the establishment of a corphin chromophore, it remains to place four "extra" methyl groups on either β-pyrrolic or *meso* positions and to ascertain the nature of the uro'gen (type I or III) whose tetramethylation generates the new corphin.

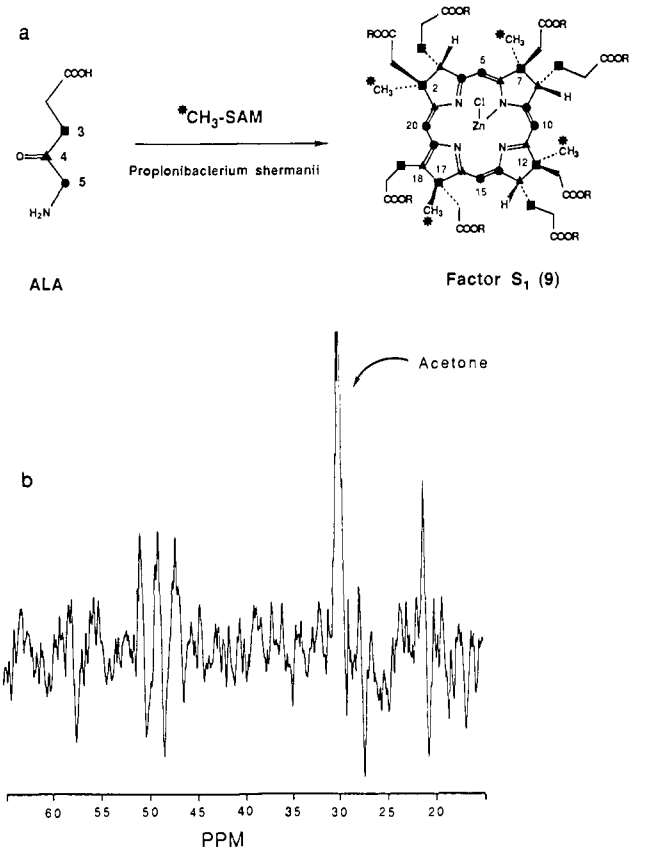


Figure 1. (a) ^{13}C-Labeling patterns in factor S_1 (R = Me) after incorporation of (*) $^{13}CH_3$-SAM and [■ 3-^{13}C]-[▲4-^{13}C] and [●5-^{13}C]-ALA in three separate experiments. (b) 75.4 MHz ^{13}C INADEQUATE spectrum of factor S_1 (100 μg) from [3-^{13}C]-ALA and $^{13}CH_3$-SAM (75.4 MHz $(CD_3)_2CO$, 20 °C) showing (*) CH_3- (■) C couplings (J = 35 Hz) for all four methyl groups ((*) CH_3; δ 16–28 ppm) at C-2, C-7, C-12, and C-17 ((■)C; 45–60 ppm). A total of 133 362 acquisitions were recorded over 16 K data points with 20 Hz exponential line broadening performed prior to transformation.

Factor S_1 was prepared from an incubation of a cell suspension[7] of *P. shermanii* containing [5-^{13}C]ALA (90% ^{13}C) and [$^{13}CH_3$]-L-Met (90% ^{13}C). The ^{13}C NMR INADEQUATE[8] spectrum of the purified octamethyl ester of factor S_1 (100 μg) shows *four pairs* of sp^2 carbons, ((●), Figure 1a) each with ^1J = 72 Hz, the hallmark of genesis from the type I **7** rather than the unsymmetrical type III structure **1** in consonance with isolation of factor S_1 from a cobalt-free incubation containing uro'gen I and SAM as the sole sources of carbon. A second isotopomer of S_1 was prepared from [4-^{13}C]-ALA and [$^{13}CH_3$]-L-Met. In this case the CMR INADEQUATE spectrum was devoid of signals indicating that none of the $^{13}CH_3$ groups (*) was present at propionate termini ((▲), Figure 1a).

To complete the structural proof, a third isotopomer of factor S_1 (100 μg) was prepared from [3-^{13}C]-ALA and [$^{13}CH_3$]-L-Met. In this case the ^{13}C-INADEQUATE spectrum (Figure 1b) of the octamethyl ester reveals *four* sp^3 carbons (■) in the region 45–60 ppm which correspond to the four *acetate* termini of the type I corphin, each of which is coupled (^1J = 35 Hz) to a methyl group derived from $^{13}CH_3$-methionine (*). In the methyl region of the spectrum (15–29 ppm) superposition of two sets of oppositely signed components of the spectrum is observed. The structure of factor S_1 is therefore **9** (R = H). The considerable line broadening in the ^{13}C NMR spectra even at −40 °C is due to tautomeric flux/ligand exchange in **9** (R = Me), an effect previously observed in the NMR spectra of the zinc corphinate **8**

(5) Factor S_1 (**9**, R = Me) has λ_{max} (rel ϵ) as follows: 302 (0.78 sh), 310 (1.00), 356 (0.85 sh), 369 (1.00), 473 (0.24 sh), 511 (0.26 sh), and 560 (0.30) nm [CH_2Cl_2].

(6) Eschenmoser, A. *Ann. N. Y. Acad. Sci.* **1986**, *471*, 108. Müller, P. M. ETH Dissertation no. 5135, **1973**, Zurich. We thank Professor Eschenmoser for spectroscopic data for the corphin **8** which has λ_{max} (rel ϵ) as follows: 293.5 (0.79 sh), 302 (1.00), 343.5 (0.85 sh) 353 (1.00), 411 (0.1), 463 (0.15 sh), 531 (0.20), and 547 (0.20) nm [EtOH].

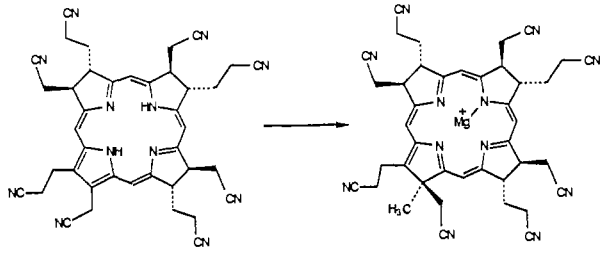
(7) See ref 4, footnote 7. Typically 100 μg of factor S_1 was obtained from 1 kg of wet cells of *P. shermanii*.

(8) Bax, A.; Freeman, R.; Kempsell, S. P. *J. Am. Chem. Soc.* **1980**, *102* 4849.

whose ^{13}C signals can only be resolved at −35 °C.[6] Thus, proof of structure for factor S_1 depends on the appearance of an "impure" spectrum at temperatures between −70 and +20 °C.[9] Unlike its isomer factor S_3,[4] which is methylated at one α-pyrrolic center, all four methyl groups in S_1 have been inserted symmetrically at the β-positions which bear acetate side chains.[10]

(9) In fact, recording the spectrum at +20 °C gave a better resolution than at −40 °C indicating that the tautomerism and/or ligand exchange is rapid at higher temperatures while at −40 °C an "impure" spectrum is observed. This is a reversal of the situation found in factor S_3[4] and the synthetic corphin[6] **8**.

(10) A striking analogy for this process is provided by a recent example of biomimetic, regioselective methylation of uro'gen I octanitrile via the tautomeric pyrrocorphin (i) to give the corphinate (ii) (as the Mg complex), where regioelectronic control favors methylation at an acetate in preference to a propionate terminus, i.e., the *exact chemical counterpart* for the biosynthesis of factor S_1. Leumann, C.; ETH Dissertation no. 8064, 1986. Leumann, C.; Früh, T.; Gobel, M.; Eschenmoser, A. *Angew Chem., Int. Ed. Engl.* **1987**, *26*, 261.



(i) (ii)

Although the stereochemistry remains to be established (since there is no biochemical correlation with cobyrinic acid), we suggest that, by analogy with cobyrinic acid (**5**), ring D is methylated at C-17 on the β-face as shown.

In summary, the structure of the second of four isomers corresponding to *nonoxidative* methylation of uro'gen I has been elucidated and takes its place as the first natural corphin isolated as its zinc complex. The fact that both factors S_1 and S_3 are natural products based on uro'gen I raises the possibility that not only are the methylases of the B_{12} pathway nonspecific[11] and able to deal with the small concentrations of the type I system (~5%) present under physiological conditions[12] but also that the intriguing opportunity now exists for the discovery of novel *corrin* structures based on a type I template. Further investigations of this topic and of the structure of the remaining isomers (factors S_2 and S_4) are in progress.

Acknowledgment. We thank N.I.H., D.F.G., the Robert A. Welch Foundation, and N.A.T.O. for generous support of this work.

(11) Nonspecific methylations are known from our unpublished studies with a partially purified C-2/C-7-methylase from *P. shermanii* which acts on uro'gen I and C-12 decarboxylated uro'gen III to yield a *type I analogue* of factor II and C-12 decarboxylated factor II, respectively. Weber, H. Dissertation, University of Stuttgart, 1981. For a recent comment on the nonspecificity of methylation of a decarboxylated uro'gen III, see: Battersby, A. R.; Bladon, C.; Huang, J.-J.; Seo, S. *J. Chem. Soc. Chem. Commun.* **1986**, 1492.

(12) HPLC analysis of the porphyrin isomer ratio (as methyl ester) in *P. shermanii* during vitamin B_{12} production (and also in the absence of cobalt) gives the ratio Uro-III 94 (±2)/Uro-I 6(±2).

Additions and Corrections

Asymmetric Synthesis of (1′*R*,3*R*,4*R*)-4-Acetoxy-3-(1′-((*tert*-butyldimethylsilyl)oxy)ethyl)-2-azetidinone and Other 3-(1′-Hydroxyethyl)-2-azetidinones from (*S*)-(+)-Ethyl 3-Hydroxybutanoate: Formal Total Synthesis of (+)-Thienamycin [*J. Am. Chem. Soc.* **1987**, *109*, 1129–1135]. GUNDA I. GEORG,* JOYDEEP KANT, and HARPAL S. GILL

Page 1135, the NMR data for compound **30** should read as follows: ^1H NMR (80 MHz) $CDCl_3$ δ 0.08 (s, 3 H, $SiCH_3$), 0.10 (s, 3 H, $SiCH_3$), 0.78 (s, 9 H, *t*-butyl), 1.32 (d, J = 6.0 Hz, 3 H, CH_3), 2.12 (s, 3 H, $COCH_3$), 3.20 (d, J = 3 Hz, 1 H, C-H_3), 3.75 (s, 3 H, OCH_3), 4.28 (dd, J = 3 and 6 Hz, 1 H, CH), 6.62 (s, 1 H, C-H_4), 6.87 (d, J = 10.4 Hz, 2 H, ArH), 7.35 (d, J = 10.4 Hz, 2 H, ArH).

Kinetics of the Thermal Reduction of Methylviologen in Alkaline Aqueous and Methanolic Solutions [*J. Am. Chem. Soc.* **1987**, *109*, 2341–2346]. VIVIAN NOVAKOVIC and MORTON Z. HOFFMAN*

Alternative mechanisms to those presented in Schemes III and IV, which satisfy the experimental rate laws and involve ion pairing explicitly, can be written.

Scheme III

$$MV^{2+} + OH^- \rightleftarrows (MV^{2+},OH^-)$$

$$(MV^{2+},OH^-) + OH^- \rightleftarrows I$$

$$I + MV^{2+} \rightarrow MV^{\bullet+} + \text{products}$$

Scheme IV

$$(MV^{2+})_2 \rightleftarrows 2\ MV^{2+}$$

$$MV^{2+} + CH_3O^- \rightleftarrows (MV^{2+},CH_3O^-)$$

$$(MV^{2+},CH_3O^-) + CH_3O^- \rightarrow I$$

$$I + MV^{2+} \rightarrow MV^{\bullet+} + \text{products}$$

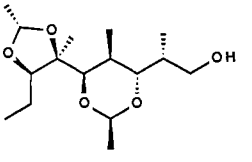
In both schemes, the products are free radicals which, as in Scheme II, can reduce MV^{2+} to yield another equivalent of $MV^{\bullet+}$, or engage in disproportionation reactions; if these secondary reactions are quantitiative, their rate constants and concentration dependences do not contribute to the overall rate law.

We thank Professor F. Scandola for directing our attention to these features of the kinetics.

Concise Total Synthesis of (+)-(9*S*)-Dihydroerythronolide A [*J. Am. Chem. Soc.* **1987**, *109*, 1565–1567]. GILBERT STORK* and SCOTT D. RYCHNOVSKY

The seventh line of the first paragraph on page 1567 should read "and its trifluoromethanesulfonic acid salt, via a syringe pump, to give macrocyclic".

The structure of the intermediate alcohol in going from **6** to **5**, depicted in the lower right corner of Scheme I, is incorrect. The correct structure is given below.



Effect of Isotopic Substitution upon the Gas Phase and Solution Electron Affinities of Nitrobenzene [*J. Am. Chem. Soc.* **1987**, *109*, 3847–3849]. GERALD R. STEVENSON,* RICHARD C. REITER,* MATTHEW E. ESPE, JOHN E. BARTMESS,* and CATHY CROWDER

Page 3847: Cathy Crowder† was inadvertently left off of the published by-line.