

**Figure 1.** Changes in rate constants of excited-state processes of crowns **1**, **2**, and **3** caused by K<sup>+</sup> (a light cation) and Cs<sup>+</sup> (a heavy cation). The arrows are to scale and represent the difference from unity of the ratio of the perturbed and unperturbed rate constants (larger rate constant taken as the numerator). An arrow pointing up indicates that the cation perturber increases the rate constant relative to that of free crown, and vice versa.

and  $k_{nr}$ ) are increased by complexed Cs<sup>+</sup> for all three crowns, and are increased relative to the values seen with K<sup>+</sup> perturbation. The postulation of Cs<sup>+</sup> enhanced spin-orbit coupling<sup>9,10</sup> in **1**, **2**, and **3** seems reasonable.

A major feature of the results is the very much larger effect of Cs<sup>+</sup> on  $k_{nr}$ ,  $k_p$ , and  $k_{dt}$  of **1** compared with **2** and **3**. Apparently, the enhancement of spin-orbit coupling is very much greater when the Cs<sup>+</sup> heavy atom is held near the face as opposed to the end or side<sup>11</sup> of the  $\pi$  system. For comparison, changes in the rate constants of **1**, **2**, and **3** caused by 20% (v/v) ethyl bromide in ethanol-methanol (4:1 v/v)<sup>12</sup> at 77 K are similar to each other, and similar to those caused by the complexed Rb<sup>+</sup> (except that ethyl bromide increases  $k_p$  of **1** three times more than Rb<sup>+</sup> does).

A second feature is that the order of susceptibility of the rate constants of **1** to Cs<sup>+</sup> ( $k_{nr} > k_p > k_{dt}$ ) is different from that found in studies of the effects of external heavy-atom perturbation of unsubstituted naphthalene. Greater susceptibility of  $k_p$  compared with  $k_{dt}$  was seen in work by Kearns,<sup>13</sup> Siegel,<sup>14</sup> and El-Sayed,<sup>15</sup> but not that of McGlynn.<sup>16</sup> However, the observation that  $k_{nr}$  of **1** is the most perturbed rate constant is consistent with the work on naphthalene by McGlynn,<sup>16,17</sup> but not that of Siegel.<sup>14</sup> The order is also different from that observed when crowns **1**, **2**, or **3** are perturbed by ethyl bromide.<sup>12</sup> In those cases  $k_p$  is increased about twice as much as  $k_{dt}$  which is only slightly more affected than  $k_{nr}$ . It is not yet clear whether the difference between Cs<sup>+</sup> perturbation of **1** and that of unoriented alkyl halides<sup>12-16</sup> is due to the added presence of a positive charge, the precise orientation<sup>18</sup> required by **1**, different thresholds of  $k_{nr}$ ,  $k_p$ , and  $k_{dt}$  to the spin-orbit perturbation, or some property of cesium.

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## References and Notes

- 1,5-Naphtho-22-crown-6 (**1**) (mp 55–56 °C) was synthesized by reaction of 1,5-bis(bromomethyl)naphthalene with pentaethylene glycol in tetrahydrofuran with potassium *tert*-butoxide.
- L. R. Sousa and J. M. Larson, presented in part at the 174th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1977.
- (a) L. R. Sousa and J. M. Larson, *J. Am. Chem. Soc.*, **99**, 307 (1977). (b) A detailed description of results with **2** and **3** has been submitted for publication.
- Quantum yields and phosphorescence lifetimes were measured in uncracked 95% ethanol glasses at 77 K with crown generally at  $1.0 \times 10^{-4}$  *F*. Fluorescence lifetimes and 77 K UV absorption spectra were measured in absolute ethanol-methanol (4:1) glasses.
- Results with NaCl, NaBr, NaI, CsCl, and CsBr show anion independence.
- The values of  $k_p$  and  $k_{dt}$  are calculated assuming that  $\phi_f + \phi_{isc} = 1.0$ : (a) V. L. Ermolaev and E. B. Sueshnikova, *Opt. Spectrosc.*, **16**, 320 (1964); (b) A. R. Horrocks and F. Wilkinson, *Proc. R. Soc. London, Ser. A.*, **306**, 257 (1968); (c) R. H. Fleming, F. H. Fleming, F. H. Quina, and G. S. Hammond, *J. Chem. Phys.*, **59**, 3433 (1973).
- With Rb<sup>+</sup> and Cs<sup>+</sup> perturbation, the  $k_f$  values (which also affect  $k_{nr}$ ) are low estimates based on a comparison of the integrated intensities of the 77 K UV absorption spectra. The approximate integrated intensities of the  $L_a$  absorptions of **1** fully complexed with Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup> relative to that of uncomplexed **1** are, respectively, 1.9:2.0:1.7:2.0:1.0.
- Attachment of the crown ring to naphthalene in the case of **1** causes relatively large changes in most rate constants compared with naphthalene which has  $k_f = 1.4 \times 10^6$ ,  $k_{nr} = 3.3 \times 10^6$ ,  $k_p = 0.017$ , and  $k_{dt} = 0.38 \text{ s}^{-1}$  under the conditions of Table I. However, complexation of Cs<sup>+</sup> by **1** causes changes in the rate constants which are clearly larger than those due to the crown substituent effect.
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- Unpublished work by James M. Larson.
- G. G. Giachino and D. R. Kearns, *J. Chem. Phys.*, **52**, 2964 (1970).
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- (a) S. P. McGlynn, J. J. Reynolds, G. W. Daigre, and N. D. Christodouleas, *J. Phys. Chem.*, **66**, 2499 (1962); (b) S. P. McGlynn, J. Daigre, and F. J. Smith, *J. Chem. Phys.*, **39**, 675 (1963).
- The order of rate constant susceptibilities is the same as that seen when naphthalene is perturbed by charge-transfer complexers (even without heavy atoms); however, there is no indication of a charge-transfer component in the emission spectra in this case. See ref 10c, p 322, and N. Christodouleas and S. P. McGlynn, *J. Chem. Phys.*, **40**, 166 (1964).
- The difference in the perturbing effectiveness of Cs<sup>+</sup> complexed by **1** as compared with **2** and **3** might in principle be rationalized by a superposition of a distance effect and some type of angular dependence (perhaps with small effects when Cs<sup>+</sup> is on the nodal plane of the  $\pi$  system). These results do not provide a separation of effects, however, since **1** allows (but does not require) Cs<sup>+</sup> to contact the  $\pi$  system while models (Corey, Pauling, Koltun) suggest that **2** and **3** hold Cs<sup>+</sup> so that 1.6 and 2.0 Å, respectively, separate the edge of the  $\pi$  system from the Cs<sup>+</sup> van der Waals radius.

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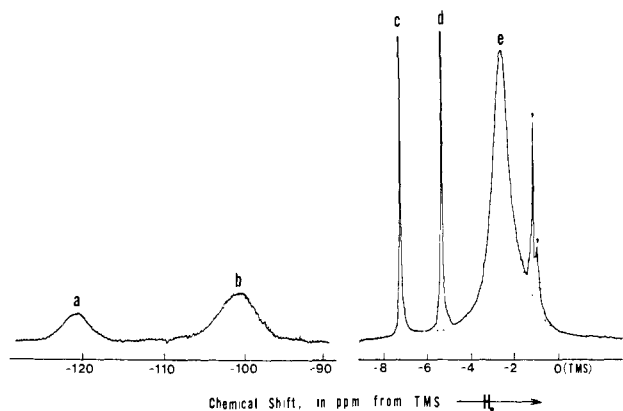
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## Structural Diversity in Iron Porphyrins: Solution Characterization of a High-Spin Six-Coordinate Ferric Complex

Sir:

The detailed characterization of solid-state structures and magnetic susceptibilities of iron porphyrin complexes in various ligation, oxidation, and spin states has produced what is generally accepted as a predictable correlation between stereochemistry and spin state that is directly applicable toward understanding certain structure-function relationships in hemoglobins.<sup>1</sup> The cornerstone of this correlation is that high-spin

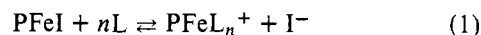


**Figure 1.**  $^1\text{H}$  NMR trace at  $-72^\circ\text{C}$  of a 3:1  $\text{C}^2\text{HCl}_3/\text{C}^2\text{H}_2\text{Cl}_2$  solution 12 mM in total porphyrin, i.e.,  $[\text{d}_{20}\text{-PFeI}]_0 = 12\text{ mM}$ , and 40 mM in total dimethyl sulfoxide, i.e.,  $[\text{L}]_0 = 40\text{ mM}$ . Peaks a and b are the pyrrole H for  $\text{d}_{20}\text{-PFeI}$  and  $\text{d}_{20}\text{-PFeL}_n^+\text{I}^-$ , respectively; c and d are the residual solvent peaks for  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$ , respectively, and e is the peak for free L at its diamagnetic position (slow exchange). Comparison of areas of e to a + b under slow ( $< -72^\circ\text{C}$ ) and fast ( $25^\circ\text{C}$ ) exchange permits direct determination of  $n$  in  $\text{d}_{20}\text{-PFeL}_n^+\text{I}^-$  via eq 2;  $x = \text{impurity}$ .

ferrous or ferric ions are too large to be accommodated within the porphyrin hole, resulting in a sizable out-of-plane displacement of the iron. The conversion of the iron to an in-plane position is invariably tied to the addition of a sixth ligand with concomitant spin pairing.<sup>2,3</sup> Thus all high-spin iron porphyrin complexes characterized to date have been found to be five coordinate.<sup>1-4</sup>

Recent theoretical considerations, however, have suggested<sup>5</sup> that nonbonded interactions between the axial ligand and the porphyrin skeleton, not the size of the high-spin iron, may be responsible for the characteristic out-of-plane displacement of the metal. Thus stable high-spin bis-ligated complexes of at least iron(III) could be expected to exist with the right choice of axial ligand. We present here direct evidence that, in the presence of certain ligands, ferric porphyrins exist solely as relatively nonlabile, high-spin bis-ligated species in solution.

The  $^1\text{H}$  NMR spectrum of (tetraphenylporphinato)iron(III) iodide,  $\text{PFeI}$ , in chloroform- $d$  and methylene chloride- $d_2$  solvents is characteristic<sup>6</sup> of the five-coordinate complex from  $-80$  to  $60^\circ\text{C}$ . Upon addition of dimethyl sulfoxide, L, to such a solution below  $-20^\circ\text{C}$ , the peak intensities of  $\text{PFeI}$  decrease and another set of resonances appears and increases in intensity at fixed position.<sup>7,8</sup> Thus only a single new species, designated  $\text{PFeL}_n^+$ , is formed according to

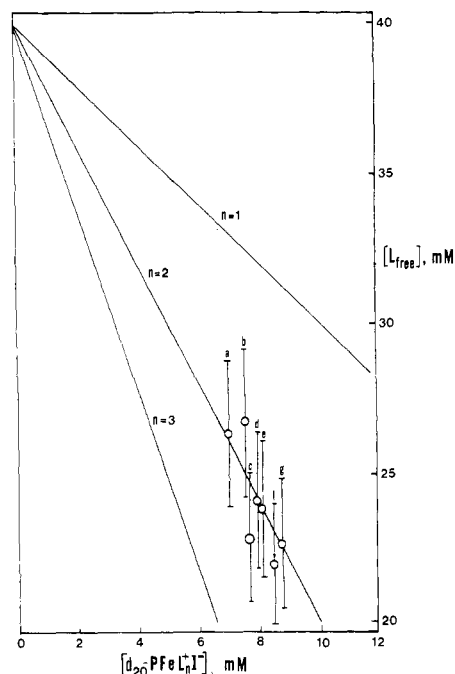


The proton trace of a  $\text{C}^2\text{HCl}_3/\text{C}^2\text{H}_2\text{Cl}_2$  solution<sup>9</sup> 40 mM in L and 12 mM in (tetraphenylporphinato)iron(III) iodide which was perdeuterated<sup>10</sup> at the phenyl positions,  $\text{d}_{20}\text{-PFeI}$ , at  $-72^\circ\text{C}$  is illustrated in Figure 1. Above  $-50^\circ\text{C}$ , the signal for L is shifted downfield and broadened with increasing amount of added L, indicating fast exchange<sup>11</sup> between free and coordinated L. Below  $-60^\circ\text{C}$ , however, the signal of free L is clearly resolved at its diamagnetic position during the addition of L, so that ligand exchange is slow on the NMR time scale.<sup>11</sup>

Although axial ligand exchange is clearly slow below  $-60^\circ\text{C}$ , the coordinated L peak is too broad to be clearly resolved.<sup>12</sup> However, the stoichiometry of the complex can be uniquely determined by monitoring the area of the various resonances in slow exchange. The simple relationship follows:<sup>13</sup>

$$[\text{L}]_{\text{free}} = [\text{L}]_0 - n[\text{d}_{20}\text{-PFeL}_n^+] \quad (2)$$

$[\text{L}]_{\text{free}}$  is obtained from the observed ratio of the area of the free L signal to the sum of the areas of the pyrrole-H peaks in  $\text{d}_{20}\text{-PFeI}$  and  $\text{d}_{20}\text{-PFeL}_n^+$ ;  $[\text{PFeL}_n^+]$  is derived from the ratio of pyrrole-H areas in  $\text{d}_{20}\text{-PFeI}$  and  $\text{d}_{20}\text{-PFeL}_n^+$ .



**Figure 2.** Plot of free dimethyl sulfoxide concentration,  $[\text{L}]_{\text{free}}$ , vs. concentration of ligated complex,  $[\text{d}_{20}\text{-PFeL}_n^+\text{I}^-]$  for the solution described in Figure 1. The straight lines correspond to solutions to eq 2 for  $n = 1, 2, \text{ or } 3$ ; the data points a-g correspond to the temperatures  $-64, -67, -68, -72, -74, -76$  and  $-78^\circ\text{C}$ , respectively.

The solutions to eq 2 for  $n = 1, 2,$  and  $3$  are depicted by lines in Figure 2, where the experimental data points in the temperature range  $-63$  to  $-78^\circ\text{C}$  are also included. It is clear from this figure that the new species must be exclusively the bis complex,  $\text{d}_{20}\text{-PFeL}_2^+\text{I}^-$ . Both solution magnetic moment ( $5.9 \pm 0.3 \mu_B$ ) and the frozen glass 77 K ESR spectrum<sup>14</sup> ( $g_{\perp} \sim 6, g_{\parallel} \sim 2$ ) dictate a pure high-spin ferric species.

Thus the dimethyl sulfoxide complex is both six coordinate and high spin in solution. Since no mono-L complex is detected, the bis complex must be more stable even though there is no spin-state change involved. Furthermore, the coordinated ligand lifetime<sup>15</sup> at  $-63^\circ\text{C}$  ( $2 \times 10^{-3}\text{ s}$ ) is comparable with that previously reported for some ferric low-spin complexes with substituted imidazoles.<sup>16</sup> The similar labilities argue against an out-of-plane displacement of the iron which would significantly enhance the lability of one of the high-spin axial ligands.

The six coordination of high-spin ferric porphyrins must account for the earlier puzzling observations<sup>8</sup> of a 80-ppm difference in meso-H shifts in chloroform and dimethyl sulfoxide solvents. Since we find the  $-40$ -ppm meso-H shifts in the presence of both dimethyl sulfoxide and dimethylformamide, the latter must also yield six-coordinate complexes. Our present results may account for the findings that five-coordinate ferric complexes are poor models for the resonance Raman spectra<sup>17</sup> of high-spin ferric hemoproteins. Since the protein iron is invariably six coordinated, we suggest that the dimethyl sulfoxide and dimethylformamide solutions should be more appropriate. The present solution NMR results, as well as crystal structural data in progress elsewhere,<sup>18</sup> indicate a more diversified spin-state/stereochemistry relationship that previously proposed, and suggest that the role of the size of the ferric ion in both model compounds and hemoproteins may have been overemphasized.

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- The sum of the pyrrole-H intensity in the two detectible species is constant; so all of the iron porphyrin exists in these two species. Furthermore, although PFeBr has a different NMR trace than PFeI, addition of dimethyl sulfoxide yields the identical species PFeL<sub>n</sub><sup>+</sup>. The optical spectra of dimethyl sulfoxide adducts of natural porphyrin complexes have also been shown to be independent of either the bromide or iodide complexes used,<sup>8</sup> indicating the lack of a coordinated halide ion in PFeL<sub>n</sub><sup>+</sup>X<sup>-</sup>.
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- The mixed solvent was used to increase the low-temperature liquid range without causing significant aggregation of the PFeI (R. V. Snyder and G. N. La Mar, *J. Am. Chem. Soc.*, **99**, 7178 (1977)).
- d*<sub>20</sub>-PFeI was required to delete the phenyl resonance of both PFeI and PFeL<sub>n</sub><sup>+</sup> so that the free L peak can be integrated quantitatively.
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- A broad (~1000 Hz) signal can be detected at ~10–12 ppm below Me<sub>4</sub>Si; however, its great width and partial overlap with solvent resonance preclude integrating it directly.
- Details of the calculation of the terms in eq 2 in terms of the signal areas, A, are as follows: [L]<sub>free</sub> = [L]<sub>0</sub>(A<sub>F</sub><sup>S</sup>/A<sub>TP</sub><sup>S</sup>)/(A<sub>F</sub><sup>L</sup>/A<sub>TP</sub><sup>L</sup>), where [L]<sub>0</sub> is the total Me<sub>2</sub>SO concentration, A<sub>F</sub><sup>L</sup> and A<sub>TP</sub><sup>L</sup> are the free Me<sub>2</sub>SO signal area and the total pyrrole-H signal area, respectively, under conditions of slow Me<sub>2</sub>SO exchange (i.e., ≤ -60 °C), while A<sub>F</sub><sup>S</sup> and A<sub>TP</sub><sup>S</sup> are the total Me<sub>2</sub>SO signal area and the total pyrrole-H signal area, respectively, under conditions of fast Me<sub>2</sub>SO exchange (i.e., ≥ -20 °C). [*d*<sub>20</sub>-PFeL<sub>n</sub><sup>+</sup>] = [P]<sub>0</sub>A<sub>F</sub><sup>S</sup>/A<sub>TP</sub><sup>S</sup>, where [P]<sub>0</sub> is the total porphyrin concentration, A<sub>F</sub><sup>S</sup> is the pyrrole-H signal area for *d*<sub>20</sub>-PFeL<sub>n</sub><sup>+</sup>, and A<sub>TP</sub><sup>S</sup> is the total pyrrole-H signal area, both under conditions of slow Me<sub>2</sub>SO exchange (≤ -60 °C).
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- Determined from broadening of free L in slow exchange.<sup>11</sup>
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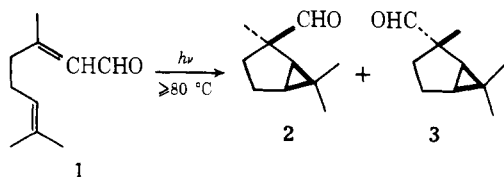
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### Novel Temperature-Dependent Photochemical Rearrangement of Citral

Sir:

In this report we describe the photochemical rearrangement of citral (**1**) to aldehydes **2** and **3** at elevated temperature. It



is noteworthy that these products are not seen at 30 °C but become increasingly important at higher temperatures and that their formation requires the unusual 1,2 shift of a formyl group. There have been rather few investigations of photochemical processes in solution at elevated temperature, and those re-

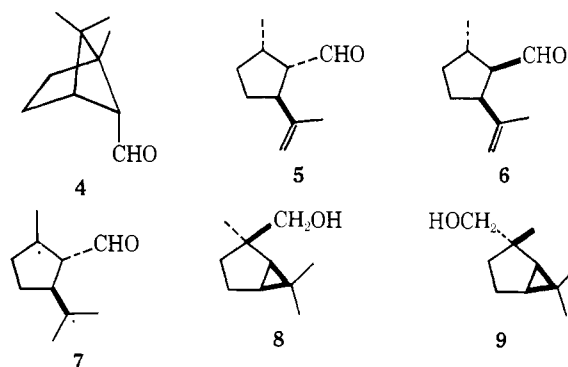
Table I. Photoisomerization of Citral at Various Temperatures

Product	Yield, %				
	30 °C	80 °C	111 °C	165 °C	190 °C
<b>2</b>	0	4	9	26	36
<b>3</b>	0	1	2	7	8
<b>4</b>	25	23	22	15	13
<b>5</b>	42	40	28	16	10
<b>6</b>	5	6	8	6	6
Total	72	74	69	70	73

ported typically concern studies below 100 °C of the kinetics or thermodynamics of processes already well known at lower temperature.<sup>1,2</sup> The present study, on the other hand, concerns photochemical transformations which require thermal activation beyond that available at room temperature.

It has been known for some years that irradiation of citral (**1**) in cyclohexane or ethanol leads in moderate yield to a mixture of photocitral B (**4**) and photocitral A (**5**), and it has been suggested that these isomers may arise through coupling and disproportionation, respectively, of the biradical intermediate **7** formed on interaction of the two olefinic double bonds of **1**.<sup>3,4</sup> We obtained similar results in benzene at 30 °C, except that we also noted the formation of 5% of a third product later shown to be **6**. Irradiation in benzene at reflux (80 °C) gave **4–6** along with 5–10% mixture of **2** and **3**. Yield data for relatively low conversion at other temperatures are shown in Table I, in which it may be seen that at 190 °C the dominant product is **2** (36%) and the combined yield of **2** and **3** is 44%, while the total yield of volatile products remains essentially constant at ~71%.<sup>5</sup>

Aldehydes **4–6** were isolated and purified by preparative vapor phase chromatography (VPC) and identified through



comparison of their properties with those previously recorded.<sup>3,4,6</sup> A mixture of **2** and **3** was obtained similarly, but no conditions tried permitted direct separation of these products. Hydride reduction of the mixture gave alcohols **8** and **9**, which could be separated by VPC and then individually oxidized back to **2** and **3** using chromium trioxide-pyridine complex.<sup>7</sup> Products **2** and **3**, as well as alcohols **8** and **9**, were fully characterized; spectroscopic data<sup>8</sup> require the formyl group and the three methyl groups of both **2** and **3** to be on quaternary carbon atoms, indicate the absence of carbon-carbon double bonds, suggest the presence of a cyclopropane ring, and point to a close structural similarity between the two isomers. These observations, together with mechanistic considerations discussed below, led to bicyclic structures **2** and **3** for these substances. Furthermore, <sup>1</sup>H NMR spectra in the presence of the lanthanide shift reagent Eu(fod)<sub>3</sub><sup>9</sup> permitted assignment of stereochemistry as shown, since in **3** one high-field (cyclopropane methine) signal moved downfield much more rapidly than in **2**.

These conclusions were verified for the major new photo-product **2** by independent synthesis from bishomocaronic acid