

paper have a high intrinsic metallic conductivity with the compressed pellet values limited by anisotropy and interparticle contacts.

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Registry No. S_4N_4 , 28950-34-7; Br_2 , 7726-95-6; ICl , 7790-99-0; IBr , 7789-33-5; $\text{SNBr}_{0.25}$, 65995-70-2; nitrogen bromide sulfide, 65995-69-9; nitrogen chloride iodide sulfide, 65995-68-8; nitrogen bromide iodide sulfide, 65995-67-7.

References and Notes

- (1) See for example, V. V. Walatka, Jr., M. M. Labes, and J. H. Perlstein, *Phys. Rev. Lett.*, **31**, 1139 (1973); C. M. Mikulski, P. J. Russo, M. S. Saran, A. G. MacDiarmid, A. F. Garito, and A. J. Heeger, *J. Am. Chem. Soc.*, **97**, 6358 (1975); R. L. Greene, G. B. Street, and L. J. Suter, *Phys. Rev. Lett.*, **34**, 577 (1975); R. H. Baughman, P. A. Apgar, R. R. Chance, A. G. MacDiarmid, and A. F. Garito, *J. Chem. Phys.*, **66**, 401 (1977); H. P. Geserich and L. Pintschovius, *Festkoerperprobleme*, **16**, 65 (1976).
- (2) M. Akhtar, J. Kleppinger, A. G. MacDiarmid, J. Milliken, M. J. Moran, C. K. Chiang, M. J. Cohen, A. J. Heeger, and D. L. Peebles, *J. Chem. Soc., Chem. Commun.*, 473 (1977); G. B. Street, W. D. Gill, R. H. Geiss, R. L. Greene, and J. J. Mayerle, *ibid.*, 407 (1977); W. D. Gill, W. Bludau, R. H. Geiss, P. M. Grant, R. L. Greene, J. J. Mayerle, and G. B. Street, *Phys. Rev. Lett.*, **38**, 1305 (1977); C. K. Chiang, M. J. Cohen, D. L. Peebles, A. J. Heeger, M. Akhtar, J. Kleppinger, A. G. MacDiarmid, J. Milliken, and M. J. Moran, *Solid State Commun.*, **23**, 607 (1977).
- (3) A. G. MacDiarmid, "Conference on Synthesis and Properties of Low-Dimensional Materials, June 13, 1977", The New York Academy of Sciences, New York, N.Y., in press, Lecture 6; M. Akhtar, C. K. Chiang, A. J. Heeger, and A. G. MacDiarmid, *J. Chem. Soc., Chem. Commun.*, 846 (1977).
- (4) G. B. Street, "Conference on Synthesis and Properties of Low-Dimensional Materials, June 13, 1977", The New York Academy of Sciences, New York, N.Y., in press, Lecture 7; G. B. Street, R. L. Bingham, J. I. Crowley, and J. Kuyper, *J. Chem. Soc., Chem. Commun.*, 464 (1977).
- (5) M. H. M. Arnold, J. A. C. Hugill, and J. M. Hutson, *J. Chem. Soc.*, 1645 (1936).
- (6) J. Bragin and M. V. Evans, *J. Chem. Phys.*, **51**, 268 (1969).
- (7) M. Becke-Goehring, *Inorg. Synth.*, **6**, 123 (1960); M. Villena-Blanco and W. L. Jolly, *ibid.*, **9**, 98 (1967).
- (8) G. Brauer, Ed., "Handbook of Preparative Inorganic Chemistry", Vol. I, 2nd ed., Academic Press, New York, N.Y., 1963, p. 275.
- (9) R. C. Weast, Ed., "Handbook of Chemistry and Physics", 50th ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1970, p. D-140.
- (10) J. Cornog and R. A. Karges, *J. Am. Chem. Soc.*, **54**, 1882 (1932).
- (11) S. Hamada, A. Takanashi, and T. Shirai, *Bull. Chem. Soc. Jpn.*, **44**, 1433 (1971).
- (12) A. Clever and W. Muthmann, *Ber. Dtsch. Chem. Ges.*, **29**, 340 (1896).
- (13) M. Goehring, *Q. Rev., Chem. Soc.*, **10**, 437 (1956); and "Ergebnisse und Probleme Chemie der Schwefelstickstoffverbindungen", Akademie-Verlag, Berlin, 1957, p. 68.
- (14) H. G. Heal, *Adv. Inorg. Chem. Radiochem.*, **15**, 375 (1972); *Inorg. Sulphur Chem.*, 459 (1968).
- (15) Z. Iqbal, R. H. Baughman, J. Kleppinger, and A. G. MacDiarmid, "Conference on Synthesis and Properties of Low-Dimensional Materials, June 13, 1977", The New York Academy of Sciences, New York, N.Y., in press, Poster Session.
- (16) M. J. Cohen, A. F. Garito, A. J. Heeger, A. G. MacDiarmid, C. M. Mikulski, M. S. Saran, and J. Kleppinger, *J. Am. Chem. Soc.*, **98**, 3844 (1976).
- (17) B. Sharma and J. Donohue, *Acta Crystallogr.*, **16**, 891 (1963).

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Effect of Para Substituent on Rates of Phenyl Ring Rotation in Gallium Complexes of Para-Substituted Tetraphenylporphyrins

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Rates of phenyl ring rotation in gallium chloro complexes of para-substituted tetraphenylporphyrins were studied by variable-temperature ^1H NMR of the phenyl resonances. Para substituents examined were trifluoromethyl, chloro, methyl, isopropyl, methoxy, and diethylamino. Activation parameters obtained by total line shape analysis are in the ranges $\Delta G^\ddagger_{298} = 12.8\text{--}15.0$ kcal/mol, $\Delta H^\ddagger = 9.2\text{--}12.5$ kcal/mol, and $\Delta S^\ddagger = -12.4$ to -8.1 eu. Rates of ring rotation for the gallium complexes are the fastest observed to date for metallotetraphenylporphyrin complexes. Rates are faster for electron-donating substituents than for electron-withdrawing substituents but do not give a linear correlation with Hammett σ_p values.

The effect of para substituent and metal ion on the rate of phenyl ring rotation in ruthenium carbonyl, indium chloro, and titanyl complexes of para-substituted tetraphenylporphyrins has been reported in a previous paper of this series.¹ Herein we report the rates of phenyl ring rotation for gallium complexes of the same series of para-substituted tetraphenylporphyrins.

Experimental Section

Physical Measurements. Infrared spectra were recorded as Nujol or halocarbon mulls on Perkin-Elmer 237 or 337 spectrophotometers. Visible spectra were obtained in chloroform solutions on Cary 14 or Beckman Acta V spectrophotometers. Data are given below with wavelengths in nm, and $\log \epsilon$ is enclosed in parentheses. ^1H NMR spectra were run at power levels well below saturation on a Varian HA-100 spectrometer equipped with a variable-temperature probe. Spectra were obtained on samples in 1:3 v/v trichloroethylene/1,1,2,2-tetrachloroethane (1:3 $\text{C}_2\text{HCl}_3/\text{C}_2\text{H}_2\text{Cl}_4$), unless otherwise noted, with the spectrometer locked on the $\text{C}_2\text{H}_2\text{Cl}_4$ resonance. ^1H NMR chemical shifts were measured with respect to $\text{C}_2\text{H}_2\text{Cl}_4$ and are reported in ppm downfield of Me_4Si using a correction of 5.96 ppm for the chemical shift of $\text{C}_2\text{H}_2\text{Cl}_4$. In order to indicate slow-exchange chemical shift differences, values of chemical shifts reported below are at -40°C , unless otherwise noted.

Preparation of Compounds. Porphyrin free bases were prepared and characterized by literature methods: $\text{H}_2(p\text{-CF}_3\text{-TPP})$;^{2,3} $\text{H}_2(p\text{-R-TPP})$, $\text{R} = \text{Cl}$, Me, OMe;^{4,5} $\text{H}_2(p\text{-i-Pr-TPP})$;⁶ $\text{H}_2(p\text{-Et}_2\text{N-TPP})$;⁷ $\text{H}_2(o\text{-Me-TPP})$.⁸

Gallium Complexes. The procedure used to synthesize the gallium complexes was analogous to that reported for the indium complexes.³ Porphyrin (0.5 mmol) and $(\text{NH}_4)_2\text{Ga}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (1.0 mmol) were refluxed in 250 mL of acetic acid containing excess sodium acetate (0.10 mol). The reaction was monitored by the disappearance of the free-porphyrin band at ca. 515 nm in the visible spectrum. When the reaction was complete, the acetic acid was removed in vacuo and the product purified by chromatography on activity IV Baker 0537 alumina. Details of reaction time, chromatography conditions, yield, and characterization data are given below for individual complexes.

$\text{Ga}(p\text{-CF}_3\text{-TPP})\text{OH}$. The reaction time was 12 h. The crude product was chromatographed on a column in CHCl_3 . Elution with CHCl_3 gave a trace of free porphyrin followed by the product. Recrystallization was from CHCl_3 /heptane; yield 84%. Visible spectrum: 400 sh (4.60), 420 (5.82), 515 sh (3.48), 551 (4.37), 590 (3.43). ^1H NMR (-40°C): pyrrole H, 9.09, singlet; $o\text{-H}$, 8.54, 8.26, doublets; $m\text{-H}$, 8.12, 8.05, doublets. Anal. Calcd for $\text{C}_{43}\text{H}_{25}\text{N}_4\text{F}_{12}\text{GaO}$: C, 59.35; H, 2.59; N, 5.77; Cl, 0.0. Found: C, 59.16; H, 2.76; N, 5.84; Cl, 0.0.

$\text{Ga}(p\text{-CF}_3\text{-TPP})\text{Cl}$. A total of 150 mg of $\text{Ga}(p\text{-CF}_3\text{-TPP})\text{OH}$ was boiled in 15 mL of $\text{C}_2\text{H}_2\text{Cl}_4$ for 3.5 h. The conversion from axial

hydroxy to axial chloro was monitored by NMR. The pyrrole H resonance in the axial chloro complex is downfield of the pyrrole H resonance in the axial hydroxy complex. Conversion was quantitative. The $C_2H_2Cl_4$ was distilled off and the product recrystallized from CH_2Cl_2 /hexane. Visible spectrum: 400 sh (4.61), 420 (5.82), 514 sh (3.44), 550 (4.36), 589 (3.39). 1H NMR ($-40^\circ C$): pyrrole H, 9.11, singlet; *o*-H, 8.48, 8.26, doublets; *m*-H, 8.10, 8.05, doublets. Anal. Calcd for $C_{48}H_{24}N_4F_{12}GaCl$: C, 58.24; H, 2.44; N, 5.66; Cl, 3.58. Found: C, 57.96; H, 2.28; N, 5.65; Cl, 3.71.

Ga(*p*-Cl-TPP)Cl. The reaction time was 7 h. The crude product was chromatographed on a column in C_2HCl_3 . A trace of free porphyrin was eluted with C_2HCl_3 , and the product was eluted with 1:5 EtOH/ C_2HCl_3 . After 1.5 h of boiling in $C_2H_2Cl_4$, the product was recrystallized from CH_2Cl_2 /hexane; yield 92%. Visible spectrum: 403 sh (4.58), 422 (5.81), 514 sh (3.48), 551 (4.37), 590 (3.61). 1H NMR ($-40^\circ C$): pyrrole H, 9.13, singlet; *o*-H, 8.26, 8.05, doublets; *m*-H, 7.79, 7.74, doublets. Anal. Calcd for $C_{44}H_{24}N_4GaCl$: C, 61.76; N, 2.83; Cl, 6.55; H, 2.83. Found: C, 61.75; H, 2.83; N, 6.59; Cl, 20.77.

Ga(*p*-Me-TPP)OH. The reaction time was 24 h. The crude complex was chromatographed on a column in C_2HCl_3 . A small amount of free porphyrin was eluted with C_2HCl_3 . The product was eluted with $CHCl_3$. Recrystallization was from CH_2Cl_2 /hexane; yield 75%. Visible spectrum: 402 sh (4.64), 423 (5.81), 515 sh (3.53), 553 (4.34), 593 (3.82). 1H NMR ($-40^\circ C$): pyrrole H, 9.16, singlet; *o*-H, 8.26, 7.99, doublets; *m*-H, 7.61, 7.53, doublets; CH_3 , 2.73, singlet. Anal. Calcd for $C_{48}H_{37}N_4GaO$: C, 76.30; H, 4.94; N, 7.42. Found: C, 76.26; H, 4.96; N, 7.43.

Ga(*p*-Me-TPP)Cl. **Ga(*p*-Me-TPP)OH** was boiled for 1 h in $C_2H_2Cl_4$. Conversion to the axial chloro complex was quantitative. Recrystallization was from CH_2Cl_2 /hexane. Visible spectrum: 402 sh (4.64), 423 (5.84), 516 sh (3.52), 552 (4.37), 592 (3.78). 1H NMR ($-40^\circ C$): pyrrole H, 9.15, singlet; *o*-H, 8.21, 7.98, doublets; *m*-H, 7.59, 7.53, doublets; CH_3 , 2.71, singlet. Anal. Calcd for $C_{48}H_{36}N_4GaCl$: C, 74.48; H, 4.69; N, 7.24; Cl, 4.58. Found: C, 74.59; H, 4.81; N, 7.17; Cl, 4.62.

Ga(*p*-*i*-Pr-TPP)Cl. The reaction time was 6 h. The crude complex was chromatographed on a column in C_2HCl_3 . A small amount of free porphyrin was eluted with C_2HCl_3 , and the product was eluted with 1:3 EtOH/ C_2HCl_3 . After 1 h of boiling in $C_2H_2Cl_4$, the product was recrystallized from CH_2Cl_2 /heptane; yield 90%. Visible spectrum: 402 sh (4.61), 423 (5.78), 515 sh (3.53), 553 (4.34), 592 (3.80). 1H NMR ($-40^\circ C$): pyrrole H, 9.17, singlet; *o*-H, 8.25, 8.01, doublets; *m*-H, 7.62, 7.56, doublets; methine H, 3.26, septet; CH_3 , 1.56, doublet. Anal. Calcd for $C_{56}H_{32}N_4GaCl$: C, 75.89; H, 5.90; N, 6.32; Cl, 4.00. Found: C, 75.62; H, 5.73; N, 6.17; Cl, 4.23.

Ga(*p*-OMe-TPP)Cl. The reaction time was 4 h. The crude product was chromatographed on a column in C_2HCl_3 . A small amount of free porphyrin was eluted with C_2HCl_3 , and the product was eluted with $CHCl_3$; yield 79%. Visible spectrum: 410 sh (4.62), 423 (5.75), 516 sh (3.57), 554 (4.34), 595 (3.91). 1H NMR ($-40^\circ C$): pyrrole H, 9.16, singlet; *o*-H, 8.24, 8.02, doublets; *m*-H, 7.30, 7.26, doublets; CH_3 , 4.10, singlet. Anal. Calcd for $C_{48}H_{36}N_4O_4GaCl$: C, 68.80; H, 4.33; N, 6.69; Cl, 4.23. Found: C, 68.84; H, 4.48; N, 6.64; Cl, 4.45.

Ga(*p*-Et₂N-TPP)Cl. The reaction time was 20 h. The crude complex was chromatographed on a column in C_2HCl_3 . Free porphyrin was eluted with C_2HCl_3 , and the product was eluted with 1:3 EtOH/ C_2HCl_3 . After 45 min of boiling in $C_2H_2Cl_4$, the product was recrystallized from CH_2Cl_2 /hexane; yield 57%. Visible spectrum: 399 (4.83), 454 (5.15), 567 (4.16), 618 (4.37). 1H NMR ($-40^\circ C$): pyrrole H, 9.25, singlet; *o*-H, 8.18, 7.96, doublets; *m*-H, 7.05, 7.01, doublets; CH_2 , 3.64, quartet; CH_3 , 1.41, triplet. Anal. Calcd for $C_{60}H_{64}N_8GaCl$: C, 71.89; H, 6.44; N, 11.18; Cl, 3.54. Found: C, 71.61; H, 6.33; N, 10.87; Cl, 3.82.

Ga(*o*-Me-TPP)Cl. The reaction time was 20 h. The crude complex was chromatographed on a column in C_2HCl_3 . A small amount of free porphyrin was eluted with C_2HCl_3 , and the product was eluted with $CHCl_3$. After 2 h of boiling in $C_2H_2Cl_4$, the product was recrystallized from CH_2Cl_2 /hexane; yield 84%. Visible spectrum: 400 sh (4.61), 421 (5.84), 512 sh (3.50), 551 (4.36), 588 (3.43). 1H NMR ($32^\circ C$, $C_2H_2Cl_4$): pyrrole H, 8.94, multiple signals; *o*-H, 8.00–8.30, multiple signals; *m*-H and *p*-H, 7.50–7.80, multiple signals; CH_3 , eight lines between 1.74 and 2.19. Anal. Calcd for $C_{48}H_{36}N_4GaCl$: C, 74.48; H, 4.69; N, 7.24; Cl, 4.58. Found: C, 74.18; H, 4.81; N, 7.30; Cl, 4.77.

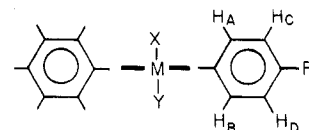
NMR Spectra. 1H NMR spectra were run on samples freshly prepared in a nitrogen atmosphere. Temperatures were calibrated after each set of data using methanol and ethylene glycol standards and the temperature-dependent shifts of Van Geet.⁹ Temperature calibrations were reproducible to $\pm 0.5^\circ C$. Temperatures are considered accurate to $\pm 1.5^\circ C$.

Computer simulations of variable-temperature 1H NMR spectra of the phenyl resonances were performed in the same fashion as previously reported for the analogous ruthenium, indium, and titanyl complexes.¹ Coupling constants for each porphyrin were within experimental error of the previously reported values.¹

Rate constants were obtained by visual comparison of calculated and observed spectra and are accurate to 8–10% except near the slow- and fast-exchange limits where uncertainties are ca. 20%. Rate constants at 10–13 temperatures were measured over intervals of 55–70 $^\circ C$ for each compound. Activation parameters were determined from weighted least-squares fits to Arrhenius ($\ln k$, vs. $1/T$) and Eyring ($\ln(hk_i/kT)$ vs. $1/T$) equations.

Results and Discussion

1H NMR Spectra. In crystal structures of metallotetraphenylporphyrins the phenyl rings are generally at angles of 60–90 $^\circ$ away from the plane of the porphyrin ring.¹⁰ For complexes with different ligands on the two sides of the metalloporphyrin plane, the ortho protons and meta protons are pairwise nonequivalent provided that both axial ligand exchange ($X \rightleftharpoons Y$) and phenyl ring rotation are slow on the



NMR time scale. At slow exchange the phenyl protons of MXY complexes of para-substituted tetraphenylporphyrins are thus an ABCD spin system. Averaging of the phenyl resonances to an AA'BB' pattern may be obtained either by rapid exchange of X and Y or by rotation of the phenyl rings with respect to the porphyrin plane. For Ga(*p*-R-TPP)X ($X = Cl, OH$) typical ABCD spectra are obtained in 1:3 C_2HCl_3 / $C_2H_2Cl_4$ at low temperatures, with the slow-exchange spectra observable at temperatures ranging from below $-40^\circ C$ ($R = Et_2N$, $X = Cl$) to below $-5^\circ C$ ($R = CF_3$, $X = OH$). At higher temperatures averaging occurs on the NMR time scale. To ascertain whether the averaging is due to axial ligand exchange or phenyl ring rotation, the 1H NMR spectra of Ga(*o*-Me-TPP)Cl were examined. As previously discussed,³ the placement of a bulky methyl group in the ortho position of the phenyl ring would be expected to greatly increase the barrier to phenyl ring rotation while having substantially less impact on the rate of axial ligand exchange. At room temperature the NMR spectrum of Ga(*o*-Me-TPP)Cl in $C_2H_2Cl_4$ solution has 8 methyl resonances between 1.74 and 2.19 ppm from Me_4Si due to the 4 possible isomers which have 12 different methyl environments.³ Thus, both phenyl ring rotation and axial ligand exchange are slow on the NMR time scale. At temperatures up to 135 $^\circ C$ there is no evidence of exchange broadening. The fact that the dynamic process which is observed between -30 and $+50^\circ C$ in the Ga(*p*-R-TPP)X complexes does not occur below $+135^\circ C$ in Ga(*o*-Me-TPP)Cl indicates that the averaging of the phenyl resonances in the former complexes is due to phenyl ring rotation and not to axial ligand exchange. Thus, computer simulation of the variable-temperature NMR spectra can provide information on the kinetics of phenyl ring rotation in the gallium complexes. The spectra as a function of temperature are similar to those shown in Figure 1 of ref 1 but with averaging occurring at lower temperatures.

Activation Parameters. Activation parameters were obtained by weighted (using the uncertainty of the rate constant) least-squares fits of the experimental rate constants to the

Table I. Activation Parameters for Phenyl Ring Rotation^a

Porphyrin	ΔG^\ddagger , kcal/mol	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , eu	E_a , kcal/mol	k_{298} , s ⁻¹
Ga(<i>p</i> -CF ₃ -TPP)Cl	14.6 ± 1.1 ^b	11.6 ± 0.8	-10.1 ± 3.0	12.1 ± 0.8	122
Ga(<i>p</i> -CF ₃ -TPP)OH	15.0 ± 1.2	12.5 ± 0.8	-8.1 ± 3.0	13.1 ± 0.8	62
Ga(<i>p</i> -Cl-TPP)Cl	14.5 ± 1.1	12.0 ± 0.8	-8.2 ± 2.8	12.6 ± 0.8	144
Ga(<i>p</i> -Me-TPP)Cl	14.2 ± 1.1	11.2 ± 0.8	-10.2 ± 3.0	11.7 ± 0.8	240
Ga(<i>p</i> -Me-TPP)OH	14.6 ± 1.4	11.3 ± 0.9	-11.2 ± 3.3	11.9 ± 0.9	122
Ga(<i>p</i> - <i>i</i> -Pr-TPP)Cl	14.0 ± 1.0	11.1 ± 0.8	-9.6 ± 2.8	11.7 ± 0.8	336
Ga(<i>p</i> -OMe-TPP)Cl	14.2 ± 1.0	10.7 ± 0.7	-11.5 ± 2.5	11.3 ± 0.7	240
Ga(<i>p</i> -Et ₂ N-TPP)Cl	12.8 ± 1.2	9.2 ± 0.8	-12.4 ± 3.0	9.6 ± 0.8	2550

^a In 1:3 C₂HCl₃/C₂H₂Cl₄ solution. ^b Uncertainties are given as ± 3 standard deviations from the least-squares lines.

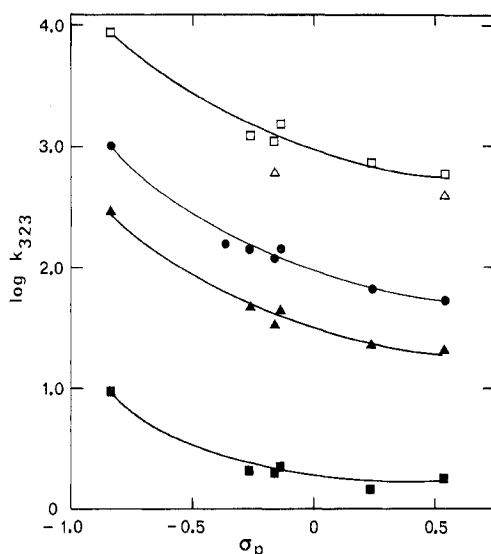


Figure 1. Plot of $\log k_{323}$ vs. Hammett σ_p for phenyl ring rotation in MXY(*p*-R-TPP): □, MXY = GaCl; △, MXY = GaOH; ●, MXY = TiO; ▲, MXY = InCl; ■, MXY = Ru(CO)(*t*-Bu(py)). The latter three sets of data are from ref 1. The lines are merely visual fits to the data and have no theoretical significance.

Arrhenius and Eyring equations. In all cases correlation coefficients of 0.995 or better were obtained. There was no evidence of deviation from linearity. Values of the activation parameters are given in Table I. Uncertainties are given as ± 3 standard deviations.

Effect of Para Substituent. The rate of phenyl ring rotation in the gallium complexes is increased by electron-donating groups and decreased by electron-withdrawing groups. As shown by the data in Table I, the rate of phenyl ring rotation in Ga(*p*-R-TPP)Cl at 298 K is about 20 times faster when R = Et₂N than when R = CF₃. Since many substituent effects in tetraphenylporphyrins have been correlated with Hammett σ values,¹ the values of the rate constants at 323 K are plotted against σ_p in Figure 1. Although considerable extrapolation of the data for the electron-donating *p*-Et₂N derivative is required to obtain k_{323} , the temperature was chosen to facilitate comparison with prior results,¹ which are also shown in Figure 1. The rates of phenyl ring rotation are not a linear function of σ_p but follow a similar pattern to the rates observed previously for the analogous Ru²⁺, TiO²⁺, and In³⁺ complexes.¹ The use of the combined equation, $\log k = a\sigma_1 + b\sigma_R$, results in correlations which are also nonlinear. The gallium complexes exhibit a sensitivity to the effect of para substituents which is quite similar to the indium and titanyl complexes and substantially greater than that for ruthenium. The ratio of the rates at 323 K for R = Et₂N and R = CF₃ are as follows: Ga³⁺, 16; TiO²⁺, 19; In³⁺, 19; Ru²⁺, 6.3.

Isokinetic Relationships. A plot of ΔH^\ddagger vs. ΔS^\ddagger is given in Figure 2 for the gallium complexes as well as the ruthenium, indium, and titanyl complexes reported in ref 1. For each

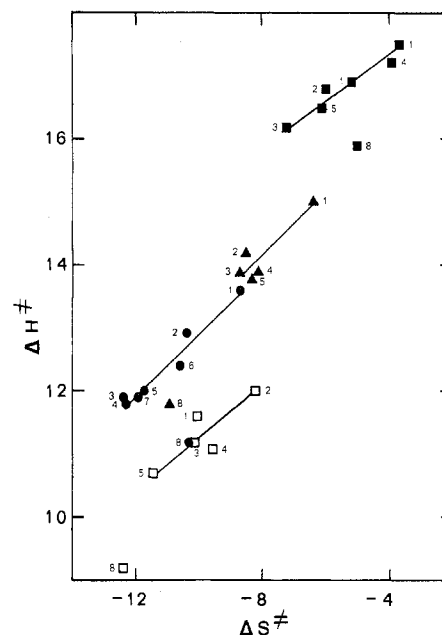


Figure 2. Plot of ΔH^\ddagger vs. ΔS^\ddagger for phenyl ring rotation in MXY(*p*-R-TPP): □, MXY = GaCl; ●, MXY = TiO; ▲, MXY = InCl; ■, MXY = Ru(CO)(*t*-Bu(py)). Numbers by data points identify R: 1, CF₃; 2, Cl; 3, Me; 4, *i*-Pr; 5, OMe; 6, *O*-*i*-Pr; 7, OH; 8, Et₂N. Lines are least-squares fits to data excluding R = Et₂N.

metal there is a reasonable correlation between ΔH^\ddagger and ΔS^\ddagger except that the point for R = Et₂N does not lie on the line defined by the other substituents. The lines in Figure 1 are least-squares fits to the data excluding R = Et₂N. Correlation coefficients are as follows: ruthenium, 0.97; indium, 0.91; titanyl, 0.97; gallium, 0.90. The deviation of the R = Et₂N point from the least-squares line implies that more than one factor is contributing to the changes in the values of ΔH^\ddagger and ΔS^\ddagger and that the relative importance of these factors is different for R = Et₂N than for the other para substituents.¹² The nonlinearity of the Hammett plots is also consistent with this conclusion.

Two factors have been proposed to contribute to the rate of biphenyl racemization: (1) bending at the 1 and/or 1' carbons and (2) conjugation between the rings.¹³ It seems reasonable that these same factors would influence the rates of phenyl ring rotation. The role of conjugation may be considerably more significant for the strongly electron-donating diethylamino group than for the other substituents.

It should also be noted that on the basis of the plots in Figure 2 the isokinetic temperature for ruthenium is lower than for the other metals studied. This observation is consistent with the decreased sensitivity of ruthenium to para substituent effects compared with other metal ions at 323 K as discussed above.

Effect of Metal Ion. As shown in Figure 1 the rates of phenyl ring rotation in the gallium complexes are markedly

faster than in the previously reported Ru^{2+} , In^{3+} , or TiO^{2+} complexes.¹ For $\text{R} = \text{Et}_2\text{N}$ the rate of phenyl ring rotation at 323 K is about 1000 times faster for $\text{MXY} = \text{GaCl}$ than for $\text{Ru}(\text{CO})(t\text{-Bu}(\text{py}))$. The electronic spectra of the gallium complexes are quite similar to those previously reported for the analogous indium and titanil complexes.¹ Since the Ga^{3+} ion is smaller than the other ions studied, it seems plausible that it would cause greater distortion of the porphyrin core when coordinated thereby facilitating ring rotation.¹ It appears that the effect of the metal ion may be largely conformational rather than electronic for these d^0 and d^{10} complexes. Crystallographic data are not available to check this hypothesis.

Effect of Axial Ligand. The rates of phenyl ring rotation in $\text{Ga}(p\text{-R-TPP})\text{X}$ with $\text{R} = \text{CH}_3$ and CF_3 are faster by about a factor of 2 for $\text{X} = \text{Cl}$ than for $\text{X} = \text{OH}$. This observation is in marked contrast to results for In^{3+} and Ru^{2+} complexes where for a limited range of axial groups the rates of phenyl ring rotation appeared to be insensitive to changes in the axial ligand.¹ It is particularly surprising that for $\text{In}(p\text{-Cl-TPP})\text{X}$ the rates of ring rotation for $\text{X} = \text{OH}$ and Cl are within about 10% but for $\text{Ga}(p\text{-R-TPP})\text{X}$, rates of ring rotation for $\text{X} = \text{OH}$ and Cl differ by about a factor of 2. Further work is necessary to assess the effect of axial ligands on rates of phenyl ring rotation.

Overall, considering the effects of metal ion and para substituents on the rate of phenyl ring rotation, the fastest rates observed to date are for $\text{Ga}(p\text{-Et}_2\text{N-TPP})\text{Cl}$. Ring rotation in this complex at 323 K is about 10^4 times faster than for $\text{Ru}(\text{CO})(p\text{-CF}_3\text{-TPP})(t\text{-Bu}(\text{py}))$ ¹ which exhibits the slowest ring rotation yet observed in a metal complex of a para-substituted tetraphenylporphyrin.

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Registry No. $\text{Ga}(p\text{-CF}_3\text{-TPP})\text{OH}$, 65930-55-4; $\text{Ga}(p\text{-CF}_3\text{-TPP})\text{Cl}$, 65930-56-5; $\text{Ga}(p\text{-Cl-TPP})\text{Cl}$, 65930-57-6; $\text{Ga}(p\text{-Me-TPP})\text{OH}$, 65930-59-8; $\text{Ga}(p\text{-Me-TPP})\text{Cl}$, 65930-60-1; $\text{Ga}(p\text{-i-Pr-TPP})\text{Cl}$, 65930-61-2; $\text{Ga}(p\text{-OMe-TPP})\text{Cl}$, 65930-62-3; $\text{Ga}(p\text{-Et}_2\text{N-TPP})\text{Cl}$, 65930-63-4; $\text{Ga}(o\text{-Me-TPP})\text{Cl}$, 65930-64-5.

References and Notes

- (1) S. S. Eaton and G. R. Eaton, *J. Am. Chem. Soc.*, **99**, 6594 (1977), and references therein.
- (2) Abbreviations used throughout: $p\text{-R-TPP}$, tetrakis($p\text{-R-phenyl}$)porphyrin dianion; $p\text{-CF}_3\text{-TPP}$, tetrakis($p\text{-(trifluoromethyl)}$)phenylporphyrin dianion; $p\text{-Cl-TPP}$, tetrakis($p\text{-chlorophenyl}$)porphyrin dianion; $p\text{-Me-TPP}$, tetrakis($p\text{-methylphenyl}$)porphyrin dianion; $p\text{-i-Pr-TPP}$, tetrakis($p\text{-isopropylphenyl}$)porphyrin dianion; $p\text{-OMe-TPP}$, tetrakis($p\text{-methoxyphenyl}$)porphyrin dianion; $p\text{-Et}_2\text{N-TPP}$, tetrakis($p\text{-(diethylamino)}$)phenylporphyrin dianion; $o\text{-Me-TPP}$, tetra- $o\text{-tolyl}$ porphyrin dianion.
- (3) S. S. Eaton and G. R. Eaton, *J. Am. Chem. Soc.*, **97**, 3660 (1975).
- (4) A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour, and L. Korsakoff, *J. Org. Chem.*, **32**, 476 (1967).
- (5) D. W. Thomas and A. E. Martell, *J. Am. Chem. Soc.*, **78**, 1338 (1956).
- (6) S. S. Eaton, G. R. Eaton, and R. H. Holm, *J. Organomet. Chem.*, **39**, 179 (1972).
- (7) N. Datta-Gupta and T. J. Bardos, *J. Heterocycl. Chem.*, **3**, 495 (1966).
- (8) A. D. Adler, L. Sklar, F. R. Longo, J. D. Finarelli, and M. G. Finarelli, *J. Heterocycl. Chem.*, **5**, 669 (1968).
- (9) A. L. Van Geet, *Anal. Chem.*, **40**, 2227 (1968).
- (10) J. L. Hoard, *Ann. N.Y. Acad. Sci.*, **206**, 18 (1973).
- (11) M. Charton, *Chemtech*, 502 (1974); 245 (1975).
- (12) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, New York, N.Y., 1963, Chapter 9.
- (13) C. C. K. Ling and M. M. Harris, *J. Chem. Soc.*, 1825 (1964).

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Coordination Sphere Flexibility at Copper: Chemistry of a Unipositive Copper(II) Macrocycle, $[\text{Cu}(\text{cyclops})]^+$

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The complex of Cu^{2+} with cyclops, an N_4 macrocycle of -1 charge, has been investigated and square-pyramidal adducts of formula $[\text{Cu}(\text{cyclops})\text{X}]$ and $[\text{Cu}(\text{cyclops})\text{L}]\text{ClO}_4$ have been isolated, where X represents a series of anionic Lewis bases and L represents a series of neutral Lewis bases. These adducts are notable for their strong axial interaction. The redox behavior of $\text{Cu}(\text{cyclops})^+$ and its adducts was studied by cyclic voltammetry, and equilibrium constants have been determined for the 1:1 interactions of both oxidized and reduced $\text{Cu}(\text{cyclops})^+$ with pyridine, γ -picoline, methyl phenyl sulfide, and benzyl isocyanide. The relationship of the chemistry of $\text{Cu}(\text{cyclops})^{+/0}$ to copper biochemistry is discussed.

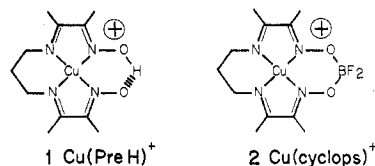
Introduction

Accelerated progress² in the field of inorganic biochemistry has stimulated the study of model systems for protein copper. Recent work has increased our appreciation of the roles of phenoxide³ and sulfur⁴⁻⁷ coordination, of tetrahedral coordination geometry,^{4,7-9} and of binucleation¹⁰ in the optical absorption³⁻⁶ and electron spin resonance⁶⁻⁸ spectroscopic and redox^{5,8-10} properties of copper proteins. Galactose oxidase¹¹ and superoxide dismutase¹² are examples of copper enzymes with "type 2" copper sites. In the latter, the copper(II) is bound to four nitrogen donors in a nearly square-planar array¹³ and is capable of binding an exogenous Lewis base in both the cuprous and cupric states.^{12,15}

We wished to synthesize a model system which might increase our understanding of type 2 copper chemistry by (a) having a nearly square-planar $(\text{Cu}^{\text{II}}\text{N}_4)^+$ chromophore as is observed in the crystal structure of the bovine dismutase,¹³ (b)

having a high affinity for one exogenous ligand in the cupric and cuprous state, and (c) exhibiting at least quasi-reversible redox behavior.

In this paper we shall discuss the chemistry of copper(II) chelates **1** and **2** and shall show that the latter system in



particular exhibits the three properties which are required of our model system.

The neutral dioxime ligand PreH_2 was first prepared by Uhlig and Friedrich¹⁶ who briefly reported on its complexes with $\text{Ni}(\text{II})$. Subsequently Gagné¹⁷ has reported the prep-