

correlation times. Similar separation in two phases, one characterized by long and the other by short correlation times of molecular motions, has been found previously by NMR for organic glasses.^{17,51,52}

The situation is depicted schematically in Figure 8d. In the rigid sites the dye molecules are more or less stuck and still characterized by an asymmetric double minimum potential of proton tautomerism, whereas in the melted regions they experience a motionally averaged symmetric double minimum potential. The latter is fundamentally different from the symmetric gas-phase potential of Figure 8a because the potential is *never* really symmetric but only on average. As shown in Figure 8e, all sites experience the same motionally averaged double minimum potential above the glass transition and can, therefore, no longer be distinguished by ¹⁵N NMR. The extension of this model to asymmetric gas-phase double minimum potentials is straightforward. Note that the glass transition was monitored by NMR at exactly the same temperature T_g as by DSC. The residual solvent and the dye molecules apparently act as additives, which are known to reduce T_g with respect to pure polystyrene.⁵¹

Conclusions

We conclude that information on fast chemical reactions under conditions of slow solvent reorientation can be obtained by solid solution state NMR. When analyzing exchange broadened NMR

spectra of bistable molecules, subject to a molecular isomerism, in the disordered solid state, inhomogeneous line broadening arising from a distribution of equilibrium constants of the isomerism has to be taken into account. We propose to use the width of the corresponding distribution function which is directly accessible by NMR as a qualitative measure of local order experienced by dyes or other additives in glasses, the crystalline state serving as a reference for perfect ordering. In addition, dyes like TTAA can also be used to indirectly monitor the motion of the surrounding molecules, which leads to a motional averaging of the double minimum potentials of the two-state exchange via exchange between the different sites. The fine details of the latter have still to be elucidated. Finally, kinetic theories of chemical reactions in condensed disordered matter have to take into account distributions of double minimum potentials with different transition state and reactant energies arising from intermolecular interactions.

Acknowledgment. We thank Dr. C. S. Yannoni and R. D. Kendrick, IBM Almaden Research Laboratory, San Jose, for their contributions to this work. The DSC measurements were kindly performed by G. Kögler, Institut für Makromolekulare Chemie der Universität Freiburg. We also thank the Deutsche Forschungsgemeinschaft, Bonn-Bad Godesberg, the Stiftung Volkswagenwerk, Hannover, and the Fonds der Chemischen Industrie, Frankfurt, for financial support.

(51) Spiess, H. W. *Coll. Pol. Sci.* **1983**, 261, 193. Wehrle, M.; Hellmann, G. P.; Spiess, H. W. *Ibid.* **1987**, 265, 815.

(52) English, A. D.; Zoller, P. *Anal. Chim. Acta* **1986**, 189, 135.

Registry No. TTAA, 116128-66-6; NiTTAA, 116651-11-0; PS, 9003-53-6; OPDA, 116006-97-4; ¹⁵NH₃, 13767-16-3; *o*-dichlorobenzene, 95-50-1; acetylacetone, 123-54-6.

⁵⁹Co NMR of Cobalt(III) Porphyrin Complexes. 2. Electric Field Gradients, d-Orbital Populations, and Hydrogen Bonding

Karen I. Hagen, Catherine M. Schwab, John O. Edwards,* John G. Jones,¹
Ronald G. Lawler, and Dwight A. Sweigart²

*Contribution from the Department of Chemistry, Brown University,
Providence, Rhode Island 02912. Received November 27, 1987*

Abstract: A series of six-coordinate cobalt(III) tetraphenylporphyrin complexes with para substituents on the phenyl groups and with a variety of axial imidazole ligands has been prepared. The ⁵⁹Co NMR spectra of these complexes in a number of solvents and at several field strengths are reported. Shielding anisotropy is very small, confirming our earlier suggestion that porphyrin, imidazole, and ammonia ligands have nearly the same position in the spectrochemical series. The chemical shift δ and line width $\omega_{1/2}$ increase as the para substituent on the TPP phenyl rings becomes electron-releasing. Correlations of δ and $\omega_{1/2}$ with Hammett σ substituent constants are noted. A simple molecular orbital model is used to rationalize both chemical shift and line width changes. It is concluded that variations in $\omega_{1/2}$ with substituent arise from changes in the electric field gradient, q , which in turn depends on the extent of mixing of metal 3d and ligand π orbitals. The chemical shift and line width also depend on the substituent on the imidazole N-1 nitrogen. In particular, hydrogen bonding to solvent or added base from axial imidazoles containing the N-H group strongly affects $\omega_{1/2}$, and the conclusion is reached that ⁵⁹Co NMR is a good way to study such "proximal" hydrogen-bonding interactions. The ⁵⁹Co NMR spectra are dominated by quadrupolar relaxation, and this is discussed along with other possible relaxation mechanisms.

⁵⁹Co NMR is relatively easy to perform and is a useful technique to probe the electronic interactions in cobalt(III) porphyrins. This, in turn, provides information that should be applicable to iron porphyrins since Co(III) has the same charge and nearly the same size as Fe(III) and is isoelectronic with low-spin Fe(II). Substituting cobalt for iron in NMR studies is particularly attractive in view of the great difficulty in obtaining ⁵⁷Fe NMR.

In a recent article we reported³ the ⁵⁹Co NMR of Co(Por)(RIm)₂⁺ complexes, where Por is the dianion of tetraphenylporphyrin (TPP) or octaethylporphyrin (OEP) and RIm is imidazole (R = H) or *N*-methylimidazole (R = Me). This work suggested that (1) ammonia, imidazole, and porphyrin ligands are very close in the spectrochemical series, (2) hydrogen bonding from the N-H hydrogen of coordinated imidazole significantly affects the chemical shift and line width, (3) substituent changes at the

(1) Permanent address: Department of Chemistry, University of Ulster, Coleraine, Northern Ireland, BT52 1SA.

(2) Recipient NIH Research Career Development Award, 1983-1988.

(3) Hagen, K. I.; Schwab, C. M.; Edwards, J. O.; Sweigart, D. A. *Inorg. Chem.* **1986**, 25, 978.

porphyrin periphery are transmitted to the metal via the ligand π -system, and (4) ⁵⁹Co and ⁵⁷Fe chemical shifts can be linearly correlated.

In this report ⁵⁹Co NMR results are presented for a series of Co(TP_xP)(RIm)₂⁺ complexes having a variety of substituents (x) on the para position of the phenyl rings and substituents (R) on the saturated imidazole nitrogen. It is shown that the shielding anisotropy is very small and that the previous conclusions about the spectrochemical series are correct. It is also demonstrated that hydrogen bonding by axial imidazole strongly affects the line widths and that ⁵⁹Co NMR is a good way to study such interactions. Hydrogen bonding of this type is believed to play an important role in hemoprotein chemistry by influencing the thermodynamics and kinetics of ligand binding, protein conformational changes, and providing a mechanism for redox potential modulation.⁴⁻²³

Experimental Section

Solvents. Solvents were ACS certified, supplied by Aldrich or Fisher, and used as received unless otherwise noted. Methanol and acetone were distilled from anhydrous calcium sulfate. Dichloromethane was distilled from P₂O₅, stored over 4A molecular sieves, and filtered prior to use. CD₃OD, CD₂Cl₂, and CDCl₃ were purchased from Cambridge Isotope Laboratory and used without purification.

Reagents. Pyrrole (Aldrich) was vacuum distilled from calcium hydride. Substituted benzaldehydes (Aldrich) were used as supplied, as were DDQ and inorganic salts. Imidazole was vacuum sublimed, and N-methylimidazole was distilled from BAO.

Chromatographic Materials. "Florosil" 100-200 mesh and "alumina adsorption (A 540)" were supplied by Fisher. Brockman grade III neutral alumina was prepared according to the directions of Nicholas.²⁴ Silicic acid (Bio A) 200-400 mesh from Bio-Rad was dried at 130 °C for 30 min and then allowed to cool in a dark desiccator over P₂O₅.

Synthesis of Cobalt Complexes. The tetraarylporphyrin ligands were prepared by the Bhatti modification²⁵ of the Rothemund reaction.²⁶ The resulting purple crystals were washed with water and dried in vacuum at 80 °C for 1 day; yields 20-25%. All preparations contained some chlorin, which was oxidized to the porphyrin with DDQ.²⁷ Cobalt was

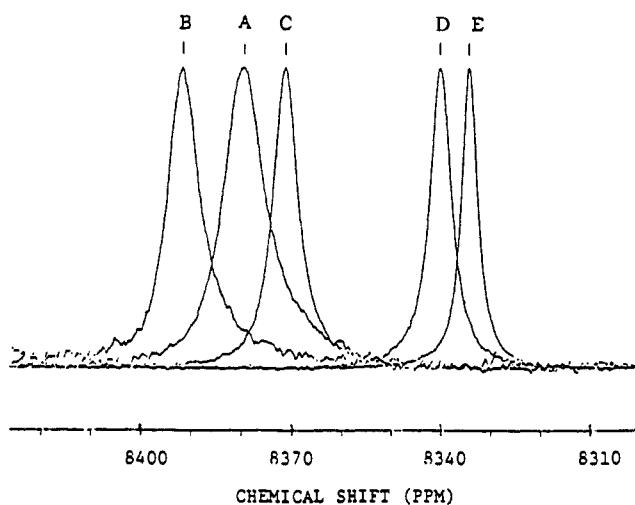


Figure 1. A computer superposition of NMR lines for five [Co(TP_xP)(N-MeIm)₂]BF₄ complexes with para substituents as follows: (A) OMe, (B) Me, (C) H, (D) Cl, (E) CF₃. All spectra were taken in MeCN at 25 ± 1 °C at 9.395 T.

Table I. Influence of Methanol on the ⁵⁹Co NMR of [Co(TPP)(RIm)₂]BF₄^a

mL of MeOH	R = CH ₃		R = H	
	δ, ppm	ω _{1/2} , Hz	δ, ppm	ω _{1/2} , Hz
0.00	8446	1000	8384	900
0.03	8442	950	8379	720
0.06	8442	950	8372	700
0.09	8441	950	8367	590
0.15	8439	950	8363	580
0.20	8438	950	8360	650
0.30	8436	1000	8356	650
3.00	8354	1000	8299	520

^a Total volume of solvent (CH₂Cl₂) and MeOH is 3.00 mL. Temperature 22.5 ± 0.5 °C.

(4) Walker, F. A.; Lo, M. W.; Ree, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 5552.

(5) Stanford, M. A.; Swartz, J. C.; Phillips, T. E.; Hoffman, B. M. *J. Am. Chem. Soc.* **1980**, *102*, 4492.

(6) Balch, A. L.; Watkins, J. J.; Doonan, D. J. *Inorg. Chem.* **1979**, *18*, 1228.

(7) O'Brien, P.; Sweigart, D. A. *Inorg. Chem.* **1985**, *24*, 1405.

(8) Poulos, T. L.; Kraut, J. *J. Biol. Chem.* **1980**, *255*, 8199.

(9) Poulos, T. L.; Freer, S. T.; Alden, R. A.; Edwards, S. L.; Skogland, U.; Takio, K.; Eriksson, B.; Xuong, N.; Yonetoni, T.; Kraut, J. *J. Biol. Chem.* **1980**, *255*, 575.

(10) Brautigan, D. L.; Feinberg, B. M.; Margoliash, E.; Peisach, J.; Blumberg, W. E. *J. Biol. Chem.* **1977**, *252*, 574.

(11) Desbois, A.; Mazza, G.; Stetzkowski, F.; Lutz, M. *Biochim. Biophys. Acta* **1984**, *785*, 161.

(12) Teraoka, J.; Kitagawa, T. *J. Biol. Chem.* **1981**, *256*, 3969.

(13) La Mar, G. N.; de Ropp, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5203.

(14) Traylor, T. G. *Acc. Chem. Res.* **1981**, *14*, 102.

(15) Valentine, J. S.; Sheridan, R. P.; Allen, L. C.; Kahn, P. C. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 1009.

(16) Morrison, M.; Schonbaum, R. *Annu. Rev. Biochem.* **1976**, *45*, 861.

(17) Stein, P.; Mitchell, M.; Spiro, T. G. *J. Am. Chem. Soc.* **1980**, *102*, 7795.

(18) Mincey, T. C.; Traylor, T. G. *J. Am. Chem. Soc.* **1979**, *101*, 765.

(19) Traylor, T. G.; Mincey, T. C.; Berzins, A. P. *J. Am. Chem. Soc.* **1981**, *103*, 7084.

(20) Shirazi, A.; Barbush, M.; Ghosh, S.; Dixon, D. W. *Inorg. Chem.* **1985**, *24*, 2495.

(21) Yoshimura, T.; Ozaki, T. *Arch. Biochem. Biophys.* **1984**, *230*, 466.

(22) Quinn, R.; Mercer-Smith, J.; Burstyn, J. N.; Valentine, J. S. *J. Am. Chem. Soc.* **1984**, *106*, 4136.

(23) Traylor, T. G.; Lee, W. A.; Stynes, D. V. *J. Am. Chem. Soc.* **1984**, *106*, 755.

(24) Nicholas, R. E. H. *Biochem. J.* **1951**, *48*, 309.

(25) Bhatti, W.; Bhatti, M.; Imbler, P.; Lee, A.; Lorenzen, B. *J. Pharm. Sci.* **1972**, *61*, 307.

(26) Rothemund, P. *J. Am. Chem. Soc.* **1935**, *57*, 2010. Rothemund, P.; Menotti, A. R. *J. Am. Chem. Soc.* **1941**, *63*, 267. Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476.

(27) Barnett, G. H.; Hudson, M. F.; Smith, K. M. *Tetrahedron Lett.* **1973**, *30*, 2887. Barnett, G. H.; Hudson, M. F.; Smith, K. M. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1401.

incorporated into the porphyrin by the method of Adler;²⁸ conversion was complete after 30 min, and crude yields were 90-95%.

The conversion of the Co(TP_xP) compounds to Co(TP_xP)(RIm)₂⁺BF₄⁻ salts was done by the method of Balch.⁶ After purification by chromatography with acetone as eluant, blue crystals were obtained by the slow addition of diethyl ether. The electronic spectra as well as ¹H and ¹³C NMR spectra correspond to those reported.²⁹ Data on electronic and NMR spectra used for identification and synthetic details are recorded in the Ph.D. theses of C.M.S. and K.I.H., Brown University (1988).

Instrumentation. ⁵⁹Co NMR spectra were obtained on a Bruker WM 250 (59.297 MHz) or a Bruker AM 400 (95.393 MHz). The NMR samples were filtered into a 10-mm tube fitted with a coaxial 5-mm tube containing the reference (0.1 M K₃Co(CN)₆) in lock solvent D₂O. The decoupler was used to maintain constant probe temperature, which was measured to ±0.1 °C on a Doric 410 A digital thermometer. On the WM 250, a pulse width of 10 μs was used, which corresponds to a pulse angle of 30°; typically 5000 transients were accumulated into 16 K data points with an acquisition time of 0.082 s. On the AM 400, a pulse width of 10 μs, corresponding to a pulse angle of 90°, was used; typically 5000 transients were accumulated into 32 K data points with an acquisition time of 0.164 s. ⁵⁹Co NMR line widths at half height (ω_{1/2}) were computed from peak shapes digitized into typically 800 points per peak. Reproducibilities for chemical shifts (δ) and line widths are discussed below.

Results

Experimental Errors. In this and an earlier study³ a large amount of chemical shift (δ) and line width (ω_{1/2}) data has been accumulated. Typical ⁵⁹Co NMR spectra are shown in Figure 1. Before discussing the numerical results, it is appropriate to

(28) Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 1443. Adler, A. D.; Longo, F. R.; Varadi, V. *Inorg. Synth.* **1976**, *16*, 213.

(29) Thomas, D. W.; Martell, A. E. *J. Am. Chem. Soc.* **1956**, *78*, 1335. Walker, F. A. *J. Am. Chem. Soc.* **1970**, *92*, 4235. Sugimoto, H.; Ueda, N.; Mori, M. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3425.

Table II. Influence of Hydrogen Bonding on the ^{59}Co NMR of $[\text{Co}(\text{TPP})(\text{HIm})_2]\text{BF}_4^a$

[phen] or [HIm]/M	δ , ppm	$\omega_{1/2}$, Hz
A. Phenanthroline ^b		
0	8389	910
3.7×10^{-3}	8389	500
1.5×10^{-2}	8387	300
3.0×10^{-2}	8385	240
6.0×10^{-2}	8386	210
B. Imidazole		
0	8390	1000
2.5×10^{-2}	8379	640
5.0×10^{-2}	8372	430
1.0×10^{-1}	8370	475

^a Conditions are CH_2Cl_2 solvent at 25.5 ± 0.5 °C and 5.872 T. ^b The addition of phenanthroline to a solution of $[\text{Co}(\text{TPP})(\text{MeIm})_2]\text{BF}_4$ did not affect δ or $\omega_{1/2}$.

consider the level of data reproducibility. The chemical shifts were usually reproducible to ± 2 ppm with occasional variations up to 4 ppm.

The precision of line width measurements was limited primarily by the ability to define the position of half-maximum and by nonreproducible temperature inhomogeneities within the sample (vide infra). Both effects give rise to errors which are a percentage of the line width. The standard deviation of a series of replicate measurements on lines having widths ranging from 200 to 2000 Hz and varying signal/noise ratios was 6%.

Temperature Effects. Chemical shifts of cobalt(III) complexes have temperature coefficients in the range of 1–2 ppm K^{-1} , so variations in line width may be due at least in part to temperature inhomogeneities in NMR tube.^{30,31} In order to check the possibility that the line width variations with changes in solvent, imidazole ligand, or phenyl ring substituent could be a consequence of systematic temperature inhomogeneities, the ^{59}Co NMR spectrum was recorded for four different $[\text{Co}(\text{TP}_x\text{P})(\text{RIm})_2]\text{BF}_4$ complexes ($x = \text{CF}_3, \text{OCH}_3$; $\text{R} = \text{H}, \text{CH}_3$) in Me_2CO and CH_2Cl_2 at 26 and 34 °C and at a field strength of 9395 T. The magnitude of $\omega_{1/2}$ ranged from 225 to 1700 Hz, and its dependence on solvent, etc. was often large but similar at both temperatures. By comparison, the dependence of $\omega_{1/2}$ on temperature for a given complex in a given solvent was found to be very small, thus excluding temperature inhomogeneity as a prime source of the line width changes found with solvent, etc. Magnetic field inhomogeneity was also shown to be insignificant (vide infra). The temperature dependence of the chemical shift, $\Delta\delta/\Delta T$, for the complexes reported herein was ca. 1.4 ppm K^{-1} , which is similar to that reported previously for other cobalt complexes.^{30,31}

Hydrogen-Bonding Effects. Our earlier study³ showed that the line widths for $\text{Co}(\text{TPP})(\text{RIm})_2^+$ have a strong solvent dependence; the same is true for the new complexes reported herein. Of particular interest is the line width difference between the HIm and MeIm complexes, which is small when the solvent has little or no donor properties (e.g., CH_2Cl_2) but is substantial with good donor solvents (e.g., Me_2CO , THF, MeOH) in which hydrogen bonding is possible involving the coordinated HIm (but not coordinated MeIm). Table I further illustrates this effect for the incremental addition of MeOH to a CH_2Cl_2 solution of $\text{Co}(\text{TPP})(\text{RIm})_2^+$. With $\text{R} = \text{Me}$, $\omega_{1/2}$ is constant; with $\text{R} = \text{H}$, a decrease in $\omega_{1/2}$ is very marked even at the 1% MeOH level.

In order to further see how hydrogen bonding influences ^{59}Co NMR chemical shifts and line widths, we recorded NMR spectra after adding various amounts of the bases phenanthroline (phen) and imidazole to $[\text{Co}(\text{TPP})(\text{HIm})_2]\text{BF}_4$. These bases are known^{6,7} to hydrogen bond to the coordinated imidazole N–H. Our results are given in Table II. In agreement with the data in Table I, the line widths decrease markedly as the hydrogen bonding be-

Table III. Selected ^{59}Co Chemical Shift and Line Width Data for Two Series of $[\text{Co}(\text{TP}_x\text{P})(\text{RIm})_2]\text{BF}_4$ Complexes^a

<i>p</i> -X	σ_p^d	series 2 ^b		series 8 ^c	
		δ , ppm	$\omega_{1/2}$, Hz	δ , ppm	$\omega_{1/2}$, Hz
OCH ₃	-0.27	8459	1580	8316	950
CH ₃	-0.17	8461	1305	8310	770
H	0.00	8447	949	8302	474
Cl	+0.23	8446	892	8297	491
CF ₃	+0.55	8438	593	8302	300
CN	+0.63	8410	573	8283	257

^a These data are for two of 13 series. A complete listing is provided as Supplementary Material. ^b Refers to $[\text{Co}(\text{TP}_x\text{P})(\text{MeIm})_2]\text{BF}_4$ in CH_2Cl_2 at 5.872 T and 24.7 ± 0.7 °C. ^c Refers to $[\text{Co}(\text{TP}_x\text{P})(\text{HIm})_2]\text{BF}_4$ in MeOH at 5.872 T and 24.7 ± 0.7 °C. ^d Hammett substituent constant.

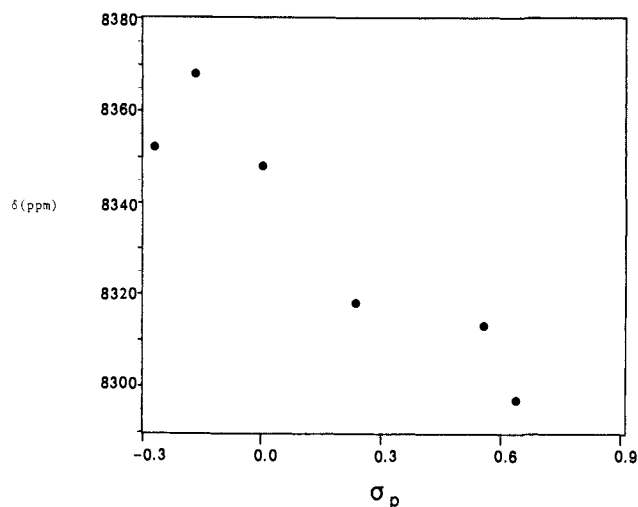


Figure 2. The chemical shift δ for six $[\text{Co}(\text{TP}_x\text{P})(\text{HIm})_2]\text{BF}_4$ complexes as a function of the Hammett σ_p constant. In order of increasing σ_p , the substituents are OMe, Me, H, Cl, CF_3 , and CN. All data were taken in MeCN at 25 ± 1 °C at 9.395 T.

comes more extensive, while, as expected, $\omega_{1/2}$ for the MeIm complex does not change with added base. In every case where a donor molecule was present (solvent or added base) the $\omega_{1/2}$ for the HIm complex was less than for the MeIm complex. Additional examples of this hydrogen bonding effect are given below.

Effect of Para Substituents on the TPP Phenyl Rings. The effect of the para substituent x in $[\text{Co}(\text{TP}_x\text{P})(\text{RIm})_2]\text{BF}_4$ was investigated by varying x from electron-withdrawing (CN, CF_3 , Cl) through H to electron-releasing (CH_3 , OCH_3) in each of 13 series of ^{59}Co NMR spectra. The series were all at 25 °C and differ in the solvent (CH_2Cl_2 , Me_2CO , MeOH, MeCN), R group (H, CH_3), and field strength (5.872, 9.395 T). Table III gives some of the results; a complete listing is provided as Supplementary Material. For each of the 13 series, the chemical shift tends to decrease as the Hammett σ_p ³² increases, i.e., δ increases as the x -group becomes more electron-releasing. This direction of δ change agrees with the conclusion reached in our previous article³ that electron release from a group on the porphyrin moves δ to a higher value. This direction of δ change was found to be the same whether the imidazole is HIm or MeIm, whether the solvent is hydrogen bonding or not, and whether the field strength is 5.872 or 9.395 T.

Although there is a clear trend, the para substituent effects on δ do not closely follow Hammett σ_p values; plots of δ versus σ_p show considerable scatter, but the scatter is not random (Figure 2). Deviations from the best line are similar for most series, e.g., δ (OCH_3) is often less than δ (CH_3), and δ (CN) is usually much less than δ (CF_3) in spite of similar σ_p values. These deviations

(30) Kidd, R. G.; Goodfellow, R. J. In *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic Press: New York, 1978; pp 225–244.

(31) Freeman, R.; Murray, Y.; Richards, R. E. *Proc. Roy. Soc.* **1957**, *A242*, 455.

(32) Jaffe, H. H. *Chem. Rev.* **1953**, *53*, 191. Gould, E. S. *Mechanism and Structure in Organic Chemistry*; Hold, Rinehart, and Winston: New York, 1959; p 221.

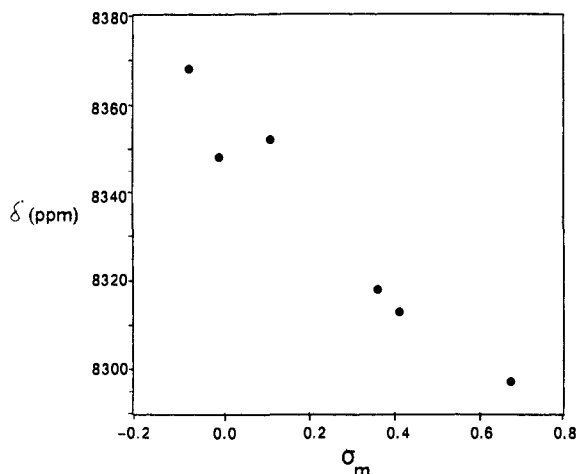


Figure 3. The chemical shift δ for six $[\text{Co}(\text{TP}_x\text{P})(\text{HIm})_2]\text{BF}_4$ complexes as a function of the Hammett σ_m constant. In order of increasing σ_m , the substituents are Me, H, OMe, Cl, CF_3 , and CN. All data were taken in MeCN at $25 \pm 1^\circ\text{C}$ at 9.395 T.

Table IV. Influence of Alkylimidazole Substituent on ⁵⁹Co NMR of $\text{Co}(\text{TPP})(\text{RIm})_2^+$ Complexes^a

substituent ^c	solvent	δ , ppm	$\omega_{1/2}$, Hz
N-CH ₃ ^b	Me ₂ CO	8409	500
N-C ₂ H ₅	Me ₂ CO	8308	650
N-C ₄ H ₉	Me ₂ CO	8280	500
N-CH ₃ ^b	MeCN	8368	500
N-C ₂ H ₅	MeCN	8277	700
N-C ₄ H ₉	MeCN	8239	560
N-CH ₃	CH ₂ Cl ₂	8446	1000
N-C ₂ H ₅	CH ₂ Cl ₂	8364	1060
N-C ₄ H ₉	CH ₂ Cl ₂	8322	840
N-CH ₃ ^b	ClCH ₂ CH ₂ Cl	8392	1600
N-C ₂ H ₅	ClCH ₂ CH ₂ Cl	8304	2200
N-C ₄ H ₉	ClCH ₂ CH ₂ Cl	8272	2000

^a Measured with a Bruker AM 400 instrument; anion is BF_4^- except where noted. Temperature of measurement: RIm = N-CH₃Im (23.3 °C), N-C₂H₅Im (24.5 °C), N-C₄H₉Im (27.3 °C). ^b Measured with a Bruker WM 250; anion is ClO_4^- .

suggest that the resonance contribution is less than that for the usual Hammett correlation. The inductive contribution in a classical organic system is measured primarily by σ_m , and a plot of δ versus σ_m is shown in Figure 3. This plot shows less scatter from a linear correlation than seen in Figure 2, but now the deviations tend to be opposite in direction, suggesting that an overcorrection was made in going from σ_p to σ_m . Details about the specific correlation type aside, the fact that the phenyl rings are roughly perpendicular to the porphyrin plane implies that π effects should not be transferred to a significant extent from the phenyls to the porphyrin π system; this is certainly what is seen.

Effect of Alkylimidazole Substituents. Varying the imidazole N-alkyl substituent in $\text{Co}(\text{TPP})(\text{RIm})_2^+$ along the series Me, Et, and Bu had no pronounced effect on $\omega_{1/2}$ but did produce a significant decrease in δ in the order Me > Et > Bu (Table IV).

Shielding Anisotropy. An important goal of the present study was to test our earlier prediction³ that there is little shielding anisotropy (SA) in the $\text{Co}(\text{TPP})(\text{RIm})_2^+$ complexes. Cobalt(III) complexes such as *trans*- $\text{Co}(\text{en})_2\text{Cl}_2^+$, which contain ligands having quite different positions in the spectrochemical series, have NMR lines which increase in line width with an increase in the magnetic field strength due to SA.³³⁻³⁵ The data obtained in the present study permitted the comparison of 39 $\omega_{1/2}$ values at 5.872 T with the corresponding values at 9.395 T. The dependence of $\omega_{1/2}$ on field strength was small and random in sign; the largest percentage difference in any $\omega_{1/2}$ pair was only 18%. A tabulation of data

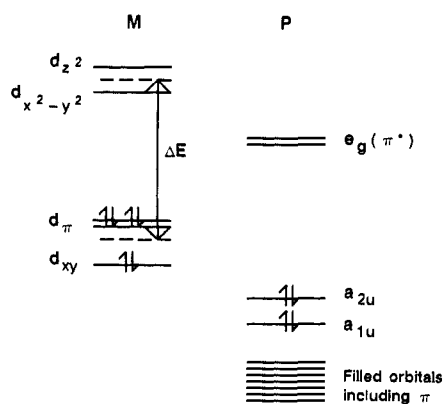


Figure 4. A schematic molecular orbital diagram for a cobalt(III) porphyrin complex with two axial ligands. Orbitals below the letter M are primarily metal based, whereas those below P are primarily porphyrin based. Axial ligand orbitals are not shown.

Table V. ⁵⁹Co NMR Line Widths^a at Various Field Strengths (B)

compound	B = 2.114 ^b	B = 5.872 T	B = 9.395 T
$\text{Co}(\text{TPP})(\text{HIm})_2^+$	1148 ^c	991	980
$\text{Co}(\text{TPP})(\text{MeIm})_2^+$	1025 ^d	949	1000

^a Units are in hertz in CH_2Cl_2 at room temperature with BF_4^- as the anion. ^b Data obtained by Dr. John Mitchell on a JEOL FX-90Q instrument. ^c Chemical shift reported^b as 8370 ppm. ^d Chemical shift reported^b as 8423 ppm.

for the two compounds $[\text{Co}(\text{TPP})(\text{RIm})_2]\text{BF}_4$ (R = H, Me) in CH_2Cl_2 at three field strengths is given in Table V. We conclude from the data that any effect due to SA is below the experimental error limit, even for complexes having smaller $\omega_{1/2}$ values (vide infra).

Discussion

Chemical Shifts. The ⁵⁹Co chemical shifts for octahedral complexes can be correlated through the Ramsey equation to the inverse of the crystal field splitting between the t_{2g} and e_g orbitals. Cobalt porphyrin complexes of the type discussed herein are close to D_{4h} symmetry, so that additional d-orbital splittings obtain. One may start with the molecular orbital calculations of Gouterman et al.,³⁶ which lead to the energy level diagram shown in Figure 4. (The metal-porphyrin bonds define the x and y axes.) The orbitals are either metal (M) or porphyrin (P) based. The axial imidazole ligands are not explicitly included, but it is unlikely that this will effect the basic conclusions because the Gouterman calculations concerned six-coordinate cobalt and related complexes.

In a $\text{Co}(\text{TP}_x\text{P})(\text{RIm})_2^+$ complex the d_{xy} orbital does not interact with the porphyrin or imidazole ligands and should, therefore, be little influenced by substituent changes at the porphyrin phenyl groups or the imidazole. The next level d_x (d_{xz} and d_{yz}) is slightly above d_{xy} and interacts with both filled and empty π orbitals on the porphyrin. The two levels d_z and $d_{x^2-y^2}$ have σ symmetry, with d_z interacting with the axial imidazoles and $d_{x^2-y^2}$ interacting with the porphyrin nitrogens. Level d_z is placed above $d_{x^2-y^2}$ in accordance with their relative placement in $\text{Fe}(\text{Por})(\text{py})_2$.³⁶ In any case it is expected that these two orbitals will be similar in energy. This conclusion follows from the fact, previously discussed,³ that $\text{Co}(\text{NH}_3)_6^{3+}$, $\text{Co}(\text{NH}_3)_5(\text{RIm})^{3+}$, and $\text{Co}(\text{TPP})(\text{RIm})_2^+$ have closely similar chemical shifts, which in turn suggests that the nitrogen ligands have nearly the same position in the spectrochemical series. The relatively narrow line widths and absence of shielding anisotropy in the ⁵⁹Co NMR of $\text{Co}(\text{TPP})(\text{RIm})_2^+$ confirm this (vide supra).

The energy labeled ΔE in Figure 4, which is the difference between the mean π -level and the mean σ -level, is an appropriate

(33) Au-Yeung, S. C. F.; Eaton, D. R. *J. Magn. Reson.* **1983**, *52*, 351.
 (34) Au-Yeung, S. C. F.; Eaton, D. R. *J. Magn. Reson.* **1983**, *52*, 366.
 (35) Au-Yeung, S. C. F.; Buist, R. J.; Eaton, D. R. *J. Magn. Reson.* **1983**, *55*, 24.

(36) Antipas, A.; Buchler, J. W.; Gouterman, M.; Smith, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 3010. Antipas, A.; Gouterman, M. *J. Am. Chem. Soc.* **1983**, *105*, 4896. Adar, F.; Gouterman, M.; Aronowitz, S. *J. Phys. Chem.* **1976**, *80*, 2184.

energy to consider for interpreting chemical shift variations. It was found (Table III, Figures 2 and 3) that electron-releasing para substituents on the phenyl rings of the TP_xP ligand generally increase the chemical shift, indicating that ΔE is decreased. Electron-releasing substituents will raise the energy of all orbitals but apparently in such a way that ΔE is decreased. This implies that the increase in electron density is transmitted to the metal mainly via the porphyrin π orbitals and not the σ orbitals. Transmission via σ -orbital interactions would be expected to lead to an increase in ΔE and a corresponding decrease in chemical shift, opposite to what was found. In a similar vein, electron-withdrawing substituents (CN, CF₃, Cl) were found to decrease δ (Table III, Figures 2 and 3).

The role of substituents on the imidazole ligands was investigated by changing the nature of the alkyl group on the 1-nitrogen. It was found that the chemical shift decreases in the order CH₃ > C₂H₅ > *n*-C₄H₉ regardless of the solvent (Table IV). This order may be compared with the Taft polar substituent constants (0.00, -0.10, and -0.13, respectively) which become more negative as the chain becomes longer.³⁷ Hence, δ decreases as the alkyl substituent becomes more electron releasing. This suggests that ΔE becomes larger, which in turn implies that the transmission of electronic effects through the imidazole ring to the cobalt is predominantly via the σ framework. An analogous effect obtains when a base is added to Co(TPP)(HIm)₂⁺ (Table III). The base hydrogen bonds to the imidazole N-H moiety, which serves to increase the electron density and decrease δ .

Line Widths. The data presented in Tables I-V and in the Supplementary Material show the following qualitative effects of substituent and medium changes on the ⁵⁹Co NMR line widths of Co(TP_xP)(RIm)₂⁺. (i) The line widths increase monotonically with the electron-donating ability of the substituent, *x*. (ii) The line widths are unaffected by changing the field strength from 5.9 to 9.4 T. They are relatively insensitive to temperature over a narrow range, with a trend toward slightly broader lines at lower temperature, and are generally narrower in solvents with low viscosity. (iii) In nonbasic solvents the line widths are remarkably insensitive to substitution at the N-1 position of the imidazole (R = H, Me, Et, *n*-Bu), in marked contrast to the large chemical shift effects observed with these substituents. In the presence of Brønsted bases, however, either as solvent or as added solute, the line widths for the imidazole complexes (R = H) decrease by factors of 2 or more while those for the alkyl-substituted imidazole series are unaffected. Below we elaborate on points (i)-(iii).

1. Substituent Effects on $\omega_{1/2}$. The mechanism by which a substituent placed at the para position of a perpendicular phenyl ring³⁸ affects an NMR line of a cobalt nucleus at the center of a porphyrin must, needless to say, be an indirect one. This strongly suggests an interaction mediated by the π , rather than the σ , framework of the porphyrin. As with most diamagnetic Co(III) complexes, relaxation is expected to be dominated by the quadrupole mechanism.³⁹ For media of low viscosity, the line width, $\omega_{1/2}$, in Hz is related to the longitudinal relaxation time, T_2 , and properties of the molecule by eq 1,⁴⁰ where $I = 7/2$ for ⁵⁹Co, q

$$\omega_{1/2} = \frac{1}{\pi T_2} = \frac{1}{\pi} \left(\frac{3}{40} \right) \left(\frac{e^2 q Q}{\hbar} \right)^2 \left(1 + \frac{\eta^2}{3} \right) \left\{ \frac{2I + 3}{I^2(2I - 1)} \right\} \tau_c \quad (1)$$

is the field gradient at the cobalt nucleus, η is the asymmetry parameter, and τ_c is the correlation time for rotational reorientation of the molecule. The cobalt porphyrin complexes are nearly axially symmetric and hence η must be very close to zero. We thus see that the quadrupolar contribution to $\omega_{1/2}$ is determined by only two variables: q and τ_c . The latter, however, is expected to be approximately proportional to the molecular volume⁴¹ and

therefore to be essentially constant for the series of complexes studied here. We conclude that variations of $\omega_{1/2}$ with substituent changes on the ligands must arise from changes in the field gradient, q .

The quantity q arises from relatively short-range interactions between the nucleus and surrounding electrons, varying as the inverse cube of the distance.⁴² It therefore seems unlikely that changes in charge distribution on the ligands can be responsible for the observed changes in $\omega_{1/2}$. It is more likely that the required alterations of charge asymmetry arise from small changes in the populations, N , of the five cobalt 3d orbitals induced by mixing between these orbitals and perturbed ligand orbitals of appropriate symmetry. The contribution to q from the 3d orbitals may be approximated by eq 2⁴³ where $\langle r^{-3} \rangle_d$ is the average value for

$$q_d = -(4/7) \langle r^{-3} \rangle_d [(N_{z^2} + N_\pi) - (N_{x^2-y^2} + N_{xy})] \quad (2)$$

a single electron in a pure cobalt 3d orbital and $N_\pi = 1/2(N_{xz} + N_{yz})$ is the average population of the two orbitals which form a degenerate pair in D_{4h} symmetry (Figure 4). Equation 2 has been written so as to emphasize the difference in population between axial (z^2 , d_π) and equatorial (x^2-y^2 , xy) 3d orbitals.

Of the five orbitals contributing to q_d only two, d_{xz} and d_{yz} , have the proper symmetry to mix with the π molecular orbitals of either the porphyrin or imidazole ligands. We therefore adopt the working hypothesis that substituent effects on $\omega_{1/2}$ arise primarily from changes in mixing between d_π (e_g) metal orbitals and π ligand orbitals of the same symmetry. The first-order mixing of d_π with filled ligand e_g orbitals should produce no net change in d orbital population. Mixing with ligand e_g (π^*), however, removes electron density from d_π thereby reducing the magnitude of N_π in eq 2. Qualitatively, electron-donating substituents, such as -CH₃ or -OCH₃, on the ligands should increase the energy of both the π^* and π ligand orbitals, moving the former further away from the d_π orbitals and the latter toward them. The energy shift of $e_g(\pi)$ may, in second-order, produce a net upward shift in the energy of d_π , as required to explain the chemical shift effect. Electron-donating substituents would also lead to decreased mixing between d_π and $e_g(\pi^*)$ and a consequent increase in the magnitude of N_π . If, in the unsubstituted complex one has $[(N_{z^2} + N_\pi) - (N_{x^2-y^2} + N_{xy})] > 0$, i.e., if there is higher electron density in the axial d orbitals than in the equatorial, an increase of N_π implies, through eq 1 and 2, an increase in the magnitude of q and a resulting increase of $\omega_{1/2}$, as observed. Since d_π interacts only weakly, and d_{xy} not at all with the ligands, one expects in general that $N_\pi < N_{xy}$. By inference, then, $N_{z^2} > N_{x^2-y^2}$. This will be true, in turn, if d_{z^2} mixes with the imidazole σ orbitals more strongly than $d_{x^2-y^2}$ mixes with the corresponding orbitals on the porphyrin. The ordering of levels shown in Figure 4 reflects this assumption.⁴⁴

2. Magnetic Field, Temperature, and Viscosity Effects. The slight decrease of $\omega_{1/2}$ with increasing temperature or decreasing viscosity over narrow ranges of these variables is in the direction predicted by the Stokes-Einstein model for τ_c ,⁴¹ eq 3. Fur-

$$\tau_c = (4\pi/3)(a^3\eta/kT) \quad (3)$$

thermore, the magnitude of τ_c may be estimated from the ¹³C relaxation time published by Huet and Gaudemer⁴⁵ for protonated carbons of the related complex Co(TPP)(py)₂⁺ in CHCl₃ at 25 °C. Assuming T_{1C} to be dominated by the dipole-dipole interaction with protons, their value of 0.2 s for this quantity and a C-H distance of 1.08 Å yields an estimate of 2.0×10^{-10} s for τ_c . The hydrodynamic radius, a , deduced via eq 3 by using this

(41) See, for example: Bartels, D. M.; Lawler, R. G.; Trifunac, A. D. *J. Chem. Phys.* **1985**, *83*, 2686.

(42) Lucken, E. A. C. *Nuclear Quadrupole Coupling Constants*; Academic Press: New York, 1969.

(43) Bancroft, G. M.; Platt, R. H. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 67.

(44) Adar, F.; Gouterman, M.; Aronowitz, S. *J. Phys. Chem.* **1976**, *80*, 2184.

(45) Huet, J.; Gaudemer, A. *Org. Magn. Reson.* **1981**, *15*, 347.

(37) Taft, R. W. In *Steric Effects in Organic Chemistry*; Newman, M. S., Ed.; John Wiley: New York, 1956; Chapter 13.

(38) Lauher, J. W.; Ibers, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 4447.

(39) Kidd, R. G. In *NMR of Newly Accessible Nuclei*; Academic Press: New York, 1983; Vol. 1, p 103.

(40) See, for example, ref 34.

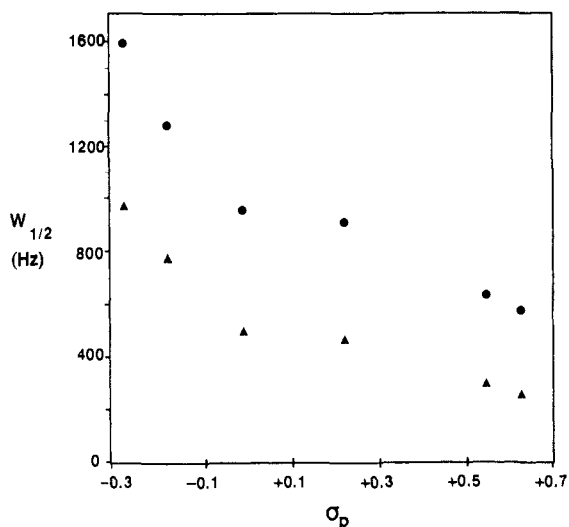


Figure 5. Line width data for [Co(TP_xP)(HIm)₂]BF₄ in MeOH (circles) and [Co(TP_xP)(MeIm)₂]BF₄ in CH₂Cl₂ (triangles) as a function of the Hammett σ_p constant. Both the circles and squares represent an average of data obtained at field strengths 5.872 and 9.395 T.

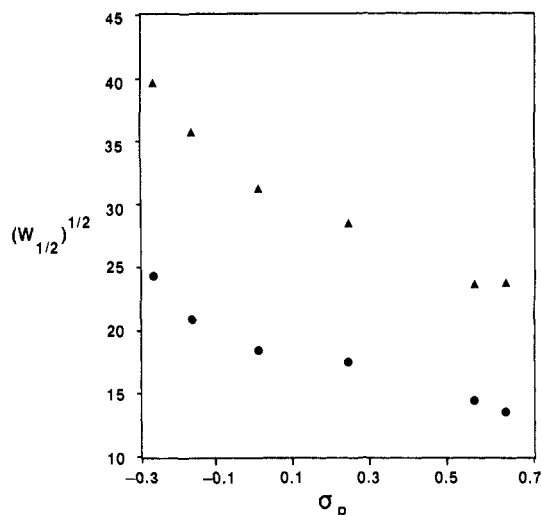


Figure 6. Square root of line width data plotted against the Hammett σ_p constant. Circles: [Co(TP_xP)(HIm)₂]BF₄ in Me₂CO; triangles: [Co(TP_xP)(HIm)₂]BF₄ in CH₂Cl₂.

value of τ_c is 7–8 Å, in accord with estimates from molecular models. This value of τ_c may also be used to derive an estimate of the quadrupole coupling constant (e^2qQ/h). For values of $\omega_{1/2}$ ranging from 200 to 2000 Hz, the approximate span of values for the cobalt porphyrin complexes with axial imidazoles, the corresponding range of values of (e^2qQ/h) are approximately 3–9 MHz. By way of comparison, the coefficient $(4/7)\langle r^{-3} \rangle_d$ in eq 2 corresponds to (e^2qQ/h) = 450 MHz for a single electron in a 3d orbital of a free Co(III) ion.⁴⁶ It is thus clear that the values of $\omega_{1/2}$ reported here are consistent with no more than a 1–2% deviation of the d orbital electron density from octahedral symmetry.

The above estimate of τ_c also makes it possible to place an upper limit on the value of the shielding anisotropy (SA), $\Delta\sigma$, for the cobalt porphyrin complexes. Thus, one has for this contribution to T_2 for an axially symmetric, isotropically tumbling complex eq 4,³³ where ω_0 is the Larmor frequency, in rad s⁻¹, in the ob-

$$1/T_2 = (7/45)\omega_0^2\Delta\sigma^2\tau_c \quad (4)$$

serving field, B_0 . Subtracting the observed T_2 's obtained at two different values of B_0 thus yields an estimate of $\Delta\sigma^2$, provided that τ_c is known. The most sensitive test of the SA contribution to T_2 in the present study is the comparison of line widths for Co(*p*-CN-TPP)(HIm)₂⁺ in MeOH at 5.9 and 9.4 T for which the tabulated line widths are 257 and 253 Hz, respectively. Assuming an error of ca. 15% (vide supra) in $\omega_{1/2}$, the SA contribution to these line widths would have to be at least 35 Hz to be reliably detected. This corresponds, via eq 4, to $\Delta\sigma < 4000$ ppm. The value of $\Delta\sigma$ is directly related to the energy difference between the $xz \rightarrow x^2-y^2$ and $d_{xy} \rightarrow [(x^2-y^2) \pm (3^{1/2}/2)z^2]$ transitions.⁴⁷ The nuclear screening parameter, σ , in ammine complexes is itself only about 18 000 ppm relative to the bare Co nucleus.⁴⁸ On the basis of this upper limit for $\Delta\sigma$, then, one can only say that the difference between the splittings of the upper and lower d states must be less than 20–30% of the overall separation of the states. Since no splitting of these states occurs for octahedral symmetry, and therefore $\Delta\sigma = 0$, this result is consistent with the conclusion that the electron density about the metal in the cobalt porphyrin complexes does not deviate appreciably from octahedral symmetry. Detection of smaller values of $\Delta\sigma$ will require complexes in which quadrupolar relaxation plays a smaller role than in those studied here.⁴⁹

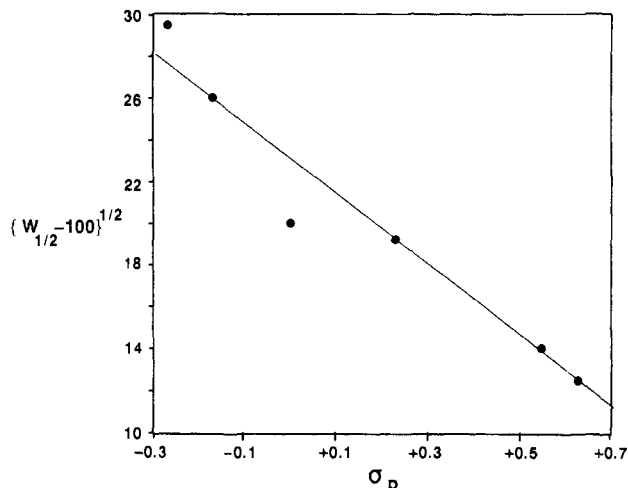


Figure 7. A plot of $(\omega_{1/2} - 100)^{1/2}$ against σ_p for [Co(TP_xP)(HIm)₂]BF₄ in MeOH. The point above the line is for OMe and that below the line is for H. The other four points are for Me, Cl, CF₃, and CN in order of increasing σ_p .

3. Correlation between $\omega_{1/2}$ and σ_p . Other Line Width Contributions. An examination of the plots of $\omega_{1/2}$ versus σ_p , such as those in Figure 5, shows that the correlation is nonlinear. If $\omega_{1/2}$ is determined exclusively by the quadrupolar relaxation mechanism, it would be expected on the basis of eq 1 that $\omega_{1/2}^{1/2}$ would serve as a measure of the electric field gradient, q , in compounds of similar structure.⁵⁰ For small substituent effects it is also reasonable to expect a linear relationship between q and measures of electron-donating ability, such as Hammett constants. A plot of $\omega_{1/2}^{1/2}$ versus σ_p (or, by implication, δ_{Co}^{51}) should therefore be linear. Such a plot is shown in Figure 6. It can be seen that the curvature is reduced relative to Figure 5 but is not completely eliminated. A plot of $\omega_{1/2}^{1/2}$ versus σ_p may be nonlinear if there are contributions to the line width other than quadrupolar relaxation. There are several other possible contributions to the line width (vide infra), and the observed $\omega_{1/2}$ may be "corrected" for these by subtracting some quantity, Y . Then a plot of $(\omega_{1/2}$

(46) Fujiwara, S.; Yajima, F.; Yamasaki, A. *J. Magn. Reson.* **1969**, *1*, 203.

(47) Juranic, N.; Celap, M. B.; Vucelic, D.; Malinar, M. J.; Radivojsa, P. *N. J. Magn. Reson.* **1979**, *35*, 319.

(48) Bramley, R.; Brorson, M.; Sargeson, A. M.; Schaffer, C. E. *J. Am. Chem. Soc.* **1985**, *107*, 2780.

(49) We have recently observed a statistically significant field effect on the line widths of the complexes with octaethylporphyrin and tetra-2,6-dichlorophenylporphyrin having HIm as axial ligands. In these instances the Co NMR lines are substantially narrower than those reported herein.

(50) Deverell, C. *Mol. Phys.* **1969**, *16*, 491.

(51) Calderazzo, F.; Lucken, E. A. C.; Williams, D. F. *J. Chem. Soc. A* **1967**, 154. Bancroft, G. M.; Clark, H. C.; Kidd, R. G.; Rake, A. T.; Spinney, H. G. *Inorg. Chem.* **1973**, *12*, 728.

$-Y)^{1/2}$ versus σ_p should be linear. Plots of this type were made (see Figure 7), and there is an improvement in linearity. Since the amount of curvature in plots like those in Figure 6 was found to be variable, it is possible to choose a different Y for each series of complexes. However, it was decided to select a single value for Y , and it was found that setting $Y = 100$ Hz produces reasonably linear plots for all 13 series of measurements. In plots like Figure 7 the points for the substituents CN, CF₃, Cl, and CH₃ fall on a straight line, but the point for -OCH₃ is always high and the point for -H always low. These two deviations from linearity are in the direction expected if the hydrodynamic radius of the complexes, and therefore τ_c , reflect the somewhat larger and smaller sizes, respectively, of these complexes. Interestingly, the "excess" line width of ca. 100 Hz is similar to the value of 66 Hz observed for $\omega_{1/2}$ for Co(OEP)(HIm)₂⁺ in THF, which is the lowest value so far found for any of the porphyrin-imidazole complexes, suggesting that in this case the simple quadrupolar mechanism makes a negligible contribution to $\omega_{1/2}$.

Of several possible additional line broadening mechanisms, we can eliminate shielding anisotropy because $\omega_{1/2}$ is not detectably field dependent (Table V). The spin-rotation interaction cannot be responsible for the Y contribution both because of the large size of the complexes and because the lines narrow slightly with increasing temperature, rather than broaden as would be expected for this mechanism.⁵² Similarly, by using Co(CN)₆³⁻, a narrow-line standard,⁵³ it was shown that instrumental sources of line broadening amount to no more than 10 Hz, i.e., about 10% of the required excess broadening.

The above considerations leave only one other common source of broadening: unresolved, but incompletely averaged, scalar coupling of the cobalt nucleus to the six ¹⁴N nuclei of the ligands. This contribution to T_2 may be written⁵⁴ according to eq 5, where

$$1/T_2 = n_s(4\pi^2/3)J^2S(S+1)T_{1N} \quad (5)$$

$n_s = 6$ is the number of ¹⁴N nuclei coupled to the cobalt, $S = 1$ is the spin of ¹⁴N, J is the scalar coupling constant between ⁵⁹Co and ¹⁴N, and T_{1N} is the spin-lattice relaxation time of ¹⁴N. Equation 5 adequately describes this contribution to T_2 only if, as expected, the resonance frequency difference between ⁵⁹Co and ¹⁴N is greater than T_{1N}^{-1} and if the cobalt spins are relaxing more slowly than the ¹⁴N spins.⁵⁵ The latter requirement is met for those complexes with the narrowest lines, where this contribution to T_2 is most important, provided that T_{1N} is less than ca. 10⁻³ s. Estimation of the scalar contribution to T_2 thus requires that we know both T_{1N} and J . Limited solubility has so far made it impossible to measure T_{1N} directly for these complexes. We may, however, estimate T_{1N} from the values of ca. 10⁻³ s published by Eaton and co-workers⁵⁵ for a series of smaller ammine complexes, assuming that the electric field gradients at the ¹⁴N nuclei are similar in the two cases and using the value of τ_c derived above for our complexes. In Eaton's case the values of τ_c were 5–10 × 10⁻¹² s, i.e., about 20 times shorter than the τ_c derived here. We therefore predict that T_{1N} for the TPP complexes should be correspondingly shorter, i.e., ca. 5 × 10⁻⁵ s.

While, in principle, we could determine J_{Co-N} directly through ¹⁵N substitution in the porphyrin and imidazole ligands, we have chosen to assume that this coupling constant differs little from the value of 45 Hz determined⁵⁶ for Co(NH₃)₆³⁺. Support for this assumption is provided by the observation⁵⁷ that $J_{^{57}Fe-^{15}N}$ is ca. 8 Hz in the porphyrin-labeled isoelectronic complex Fe(TPP)(py)₂. Correcting for the relative sizes of the ⁵⁷Fe/⁵⁹Co and ¹⁵N/¹⁴N magnetogyric ratio pairs yields an estimate of 40 Hz for the coupling between the cobalt nucleus and the porphyrin

¹⁴N nuclei. Substitution of the above estimates of J and T_{1N} into eq 5 yields a value of ca. 0.05 s for the scalar contribution to T_2 . This corresponds to a 5-Hz contribution to $\omega_{1/2}$, or only about 5% of the excess line width. We must therefore look elsewhere for an explanation of this effect.

Virtually the only remaining plausible contribution to $\omega_{1/2}$ for ⁵⁹Co which would not be correlated directly with rotational motion and a static field gradient is the well-documented, but poorly understood, dynamic quadrupolar relaxation mechanism.⁵⁸ This has been invoked to explain line width variations in nominally octahedral complexes for which the average field gradient at the cobalt nucleus should be zero.⁵⁹ This effect seems to increase, at least qualitatively, with the overall size of the complex and might be especially important for large ligands such as TPP. It is also tempting to ascribe to this effect some of the line width variation, particularly narrowing which seems to accompany increased electron donation by the imidazole ligands, either by alkyl group substitution or hydrogen bonding (vide infra).

4. Line Width Effects of Hydrogen Bonding and Imidazole Substituents. The formation of hydrogen bonds and the change in alkyl substituents to larger groups both make the axial ligands more electron releasing. However, the line width variations are not identical; hydrogen bonding brings about a factor of two (or more) drop in $\omega_{1/2}$, whereas a change in alkyl group from methyl to ethyl and on to *n*-butyl results first in an increase in $\omega_{1/2}$ followed by a decrease. The trend with alkyl group seems consistent (see Table IV), and in some instances, as in the change from methyl to ethyl in MeCN, the difference in $\omega_{1/2}$ values is outside the experimental error. The interpretation of these line widths is complicated by the fact that electron donation is common to both types of change but observed $\omega_{1/2}$ effects are at least qualitatively different.

It might be expected that the model used to explain TPP substituent effects on $\omega_{1/2}$ and δ_{Co} could also be used to predict the line width effects of added base (hydrogen bonding) or alkyl substitution at the N-1 of the imidazole ligand. The decrease of δ_{Co} in this case, requiring an increase of ΔE , is in fact consistent with an extension of this model in which there is a significant upward shift of d_z accompanying increased mixing between this d orbital and a destabilized unshared pair of electrons on N-3 of the imidazole. This effect, operating predominantly through the σ -electrons of imidazole, might reasonably be larger than the related upward shift of d_x arising from decreased interaction with the $e_g(\pi^*)$ orbitals of imidazole. The σ -shift would thus dominate and ΔE increase, as observed.

Unfortunately, a serious contradiction is encountered when this model is applied to predict q_d and therefore $\omega_{1/2}$. The upward shift of the unfilled d_z orbital implies an increase in the mixing between the filled imidazole σ orbitals and d_z and, therefore, an increase in the population, N_{d_z} , of this d orbital. Similarly, the increased energy of the d_x orbital arising from decreased mixing with the $e_g(\pi^*)$ orbitals should be accompanied, as in the case of TPP substituents, by an increase in population of the d_x orbitals. Inasmuch as the populations of the $d_{x^2-y^2}$ and d_{xy} orbitals should be unaffected by axial ligand substitution, the net result, via eq 2, should be an increase of q_d , and, therefore, of $\omega_{1/2}$, in contrast to the observations. Furthermore, one cannot invoke changes in τ_c to explain the effect because substitution or hydrogen bonding should increase the size of the complex, lengthening τ_c and broadening the lines.

We are unable at present to suggest a modification of the above qualitative model which would predict simultaneously the effects on $\omega_{1/2}$ and δ_{Co} without making unreasonable assumptions about the relative zeroth-order energies of the cobalt and imidazole orbitals. One such modification, for example, would require the unshared pairs of the imidazole to have a higher energy than the

(52) Hubbard, P. S. *Phys. Rev.* **1963**, *131*, 1155.

(53) Eaton, D. R.; Rogerson, C. V.; Sandercock, A. C. *J. Phys. Chem.* **1982**, *86*, 1365.

(54) Abragam, A. *The Principles of Nuclear Magnetism*; Oxford University Press: London, 1961; Chapter 8.

(55) Rose, K. D.; Bryant, R. G. *Inorg. Chem.* **1979**, *18*, 1332.

(56) Jordon, R. B. *J. Magn. Reson.* **1980**, *38*, 267.

(57) Nozawa, T.; Sato, M.; Hatano, M.; Kobayashi, N.; Osa, T. *Chem. Lett.* **1983**, 1289.

(58) Valiev, K. A. *Soc. Phys. JETP* **1960**, *37*, 77.

(59) Doddrell, D. M.; Bendall, M. R.; Healy, P. C.; Smith, G.; Kennard, C. H. L.; Reston, C. L.; White, A. H. *Aust. J. Chem.* **1979**, *32*, 1219. Doddrell, D. M.; Bendall, M. R.; O'Connor, A. J.; Pegg, D. T. *Aust. J. Chem.* **1977**, *30*, 943. But also see: Grahn, H.; Edlund, V.; Holak, T. A. *Magn. Reson. Chem.* **1987**, *25*, 497.

3d orbitals of Co(III), a conjecture unsupported by any other evidence of which we are aware. The dynamic quadrupolar relaxation mechanism mentioned above may provide an explanation for some of the line width observations. Hydrogen bonding is a very rapid dynamic effect and might contribute in this way to the relaxation. Also, rotation of the imidazole ligands about the cobalt–nitrogen bond axis could cause a dynamic relaxation; apparently the potential barrier to such rotation is small.⁶⁰ These effects, as well as other puzzling ⁵⁹Co line width effects involving other substituted porphyrin and imidazole ligands⁶¹ merit further investigation.

Acknowledgment. We are grateful to the National Institutes of Health for supporting the research (Grant no. DK30145), to Brown University for an University Fellowship to C.M.S., to Dr.

James Van Epp for NMR technical assistance, to Dr. John Mitchell for line width data at 2.114 T, and to Drs. Paul O'Brien, Luigi Cassidei, Philip Rieger, and W. Robert Scheidt for helpful discussions.

Supplementary Material Available: Tables giving the influence of temperature on ⁵⁹Co NMR and the experimental conditions for ⁵⁹Co NMR studies of [Co(TP_xP)(RIm)₂]BF₄ and substituent effects on ⁵⁹Co chemical shifts and ⁵⁹Co line widths (4 pages). Ordering information is given on any current masthead page.

(60) Scheidt, W. R.; Chipman, D. M. *J. Am. Chem. Soc.* **1986**, *108*, 1163.

(61) Schwab, C. M.; Hagen, K. I.; Cassidei, L.; Edwards, J. O., to be published.

Estimation of the H–H Distances of η^2 -Dihydrogen Ligands in the Complexes $trans\text{-}[M(\eta^2\text{-H}_2)(\text{H})(\text{PR}_2\text{CH}_2\text{CH}_2\text{PR}_2)_2]^+$ [M = Fe, Ru, R = Ph; M = Os, R = Et] by Solution NMR Methods

Maria T. Bautista, Kelly A. Earl, Patricia A. Maltby, Robert H. Morris,*
Caroline T. Schweitzer, and Andrea Sella

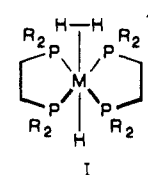
Contribution from the Department of Chemistry and the Scarborough Campus, University of Toronto, Toronto, Ontario M5S 1A1, Canada. Received February 9, 1988

Abstract: The spin–lattice relaxation times, T_1 , of the dihydrogen and hydride ligands in the complexes $trans\text{-}[M(\eta^2\text{-H}_2)(\text{H})(\text{PR}_2\text{CH}_2\text{CH}_2\text{PR}_2)_2]^+$ [M = Fe, Ru, R = Ph; M = Fe, R = C₆D₅; M = Os, R = Et] have been measured as a function of temperature by the ¹H NMR inversion–recovery method. The equations for dipolar relaxation fit the data fairly well, and from them the correlation time parameter τ_0 and the activation energy parameter E_a are obtained for the equation $\tau_H = \tau_0 e^{E_a/RT}$ where τ_H is the correlation time of the hydride ligand. It is necessary to take into account that the T_1 values average once intramolecular exchange occurs between the H and H₂ hydrogens. Reasonable H–H distances for the H₂ ligands are obtained if Woessner's relaxation equation is used, which applies for the case when the correlation time of this ligand is much shorter than that of the terminal hydride because of rapid rotation about the M–H₂ bond: for the Fe complex, 0.86 ± 0.02 Å; for Ru, 0.89 ± 0.02 Å; and for Os, 1.12 ± 0.03 Å. For the Os complex it is not possible to rule out the possibility that there is restricted rotation of the H₂ ligand because of a strong Os–H₂ interaction; in this case the H–H distance could be as long as 1.40 Å. Tunneling of H atoms between sites of approximately C_{4v} symmetry could also account for the internal motion. Calculated T_2 values do not account for breadth of the H₂ resonances in some cases.

Crabtree and Hamilton¹ have recently described how T_1 measurements can be used to determine the H–H distances of η^2 -dihydrogen ligands² in transition-metal complexes in solution. The success of the method relies on the fact that dipolar relaxation is almost solely responsible for the short T_1 values measured for η^2 -H₂ ligands because of the close proximity of one H to the other.³ However, H–H distances determined by neutron² and X-ray⁴ diffraction methods were found to be shorter by a correction factor (C) of about 0.9 relative to the distances calculated from the T_1 data.^{1a} We describe here spin–lattice relaxation time measurements on our iron-group molecular hydrogen complexes,^{4,5} which

suggest that the correction factor should be 0.794 and it arises because of the rotational motion of the H₂ ligand in the complex.

We have previously reported NMR studies to order the H–H distances in the complexes $trans\text{-}[M(\eta^2\text{-H}_2)(\text{H})(\text{dppe})_2]\text{BF}_4$, M = Fe (**1Fe**) and Ru (**1Ru**) and dppe = PPh₂CH₂CH₂PPh₂, and the complexes $trans\text{-}[M(\eta^2\text{-H}_2)(\text{H})(\text{depe})_2]\text{BPh}_4$, with M = Fe (**2Fe**), Ru (**2Ru**), and Os (**2Os**) and depe = PET₂CH₂CH₂PET₂.^{5a} The trend uncovered based on single T_1 determinations and ¹J-(H,D) coupling constants was that the H–H bonds lengthen as Ru < Fe < Os. The complexes have a trans structure I at low temperatures, but at higher temperatures hydrogen atom exchange between the terminal hydride and dihydrogen ligands occurs.



(1) (a) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126–4133. (b) Crabtree, R. H. Presented at the 3rd International Conference on the Platinum Metals, Royal Society of Chemistry, Sheffield, July 1987. (c) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299–338.

(2) (a) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. (b) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451–452. (c) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000–7009. (d) Wasserman, H. J.; Kubas, G. J.; Ryan, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2294–2301.

(3) (a) Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032–4037. (b) Crabtree, R. H.; Hamilton, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 3124–3125.

(4) Morris, R. H.; Sawyer, J. F.; Shiralian, M.; Zubkowski, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5581–5582.

(5) (a) Bautista, M.; Earl, K. A.; Morris, R. H.; Sella, A. *J. Am. Chem. Soc.* **1987**, *109*, 3780–3782. (b) Bautista, M. T.; Earl, K. A.; Morris, R. H. *Inorg. Chem.* **1988**, *27*, 1124–1126. (c) Bautista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4056–4057. (d) Morris, R. H.; Earl, K. A.; Luck, R. L.; Lazarowich, N. J.; Sella, A. *Inorg. Chem.* **1987**, *26*, 2674–2683.