study. Furthermore, the evidence that we have identified the correct geometry for this species is circumstantial at best since we cannot allow for the charge and did not observe the sequential formation of *trans*- and then *cis*-$[Pt(Xpy)(Me_2SO)Cl_2]$.

Further studies are needed to evaluate the effects of ortho oxo groups and charge on ^{195}Pt NMR shifts. Also, since the effects of the nonvaried ligands on Pt may modulate the effects of the heterocyclic N-donor ligands on the ^{195}Pt NMR shifts, several additional series need to be investigated to confirm the generality of the nonbonded effects on shifts reported here.

Acknowledgment. We thank the NIH for support through Grant GM 29222 and Matthey Bishop, Inc., for a loan of $K_2[PtCl_4]$. We also thank the NSF for partial support of the purchase of the 360-MHz spectrometer and the EURC for partial support.

Contribution from the Department of Chemistry,
Brown University, Providence, Rhode Island 02912

Application of ^{59}Co NMR to Cobalt(III) Porphyrins. Linear Relationship between ^{59}Co and ^{57}Fe Chemical Shifts

Karen I. Hagen, Catherine M. Schwab, John O. Edwards,* and Dwight A. Sweigart[1]

Received October 28, 1985

The ^{59}Co NMR spectra have been recorded for various cobalt(III) complexes: $Co(NH_3)_5L^{3+}$ and $Co(por)L_2^+$, where L = imidazole (HIm), *N*-methylimidazole (MeIm), pyridine, and ammonia and por = dianion of tetraphenylporphyrin (TPP) and octaethylporphyrin (OEP). Chemical shift and line width data suggest that ammonia, imidazole, and porphyrin ligands are very close in the spectrochemical series. It seems that ^{59}Co NMR is more sensitive than optical spectroscopy for placing ligands in the spectrochemical series and should prove useful for predicting d–d excitation energies for complexes in which allowed bands obscure these transitions. Hydrogen bonding by axial imidazole in $Co(por)(HIm)_2^+$ to solvent or external base influences the chemical shift and line width. A linear correlation between ^{59}Co and ^{57}Fe chemical shifts is postulated that depends on a simplified Ramsey equation in which the chemical shift is determined principally by the lowest energy d–d excitation; this correlation may be useful for predicting ^{57}Fe chemical shifts in iron(II) porphyrins and other iron complexes. Two shiftability ratios (0.57 for Fe/Co and 1.16 for Mo/V) have been estimated.

NMR on the iron nucleus is a difficult and tedious task because the only naturally occurring isotope with a nonzero spin, ^{57}Fe ($I = {}^1/_2$, 2.19% abundance), has a very low receptivity and long relaxation time. Accordingly, there are few data on ^{57}Fe chemical shifts in the literature. Cobalt, on the other hand, exists as 100% ^{59}Co ($I = {}^7/_2$; $Q = 0.40$ b) and has a receptivity 4×10^5 times larger than for iron. Therefore, ^{59}Co NMR is easily performed and a considerable volume of data exists.[2-4] In this paper we show that the ^{57}Fe chemical shift in a given complex can be predicted from the ^{59}Co chemical shift in the corresponding isoelectronic cobalt complex. This discovery should prove to be of significance in a number of areas of iron chemistry, including iron porphyrins and proteins.

The present study has two purposes. In one, we investigated the ^{59}Co NMR of cobalt(III) porphyrins with a variety of axial ligands in the hope of learning about hydrogen bonding to/from the axial ligands. Such hydrogen bonding is known[5-8] to influence stability constants, reactivities, and redox potentials of simple iron porphyrins. Similarly, hydrogen bonding from the distal histidine in Hb and Mb is known[9-11] to affect O_2 binding and stability to autoxidation. Hydrogen bonding from the metal-bound proximal histidine is thought[12] to provide a mechanism by which some heme proteins can modulate their metal-centered redox potentials.

The second purpose of this study is related to the NMR of cobalt and iron compounds. Cobalt porphyrins under proper circumstances can be good model systems to learn about iron porphyrin behavior; cobalt(III) is isoelectronic with iron(II) and has the same charge as iron(III). It was felt that a study of ^{59}Co NMR in ammine and porphyrin complexes, particularly ones with axial imidazole ligands, would provide information about metal–ligand interactions that could be transferred to the iron systems. To the best of our knowledge, no ^{59}Co NMR studies of porphyrins have been made. Herein we present data for a variety of cobalt ammine and porphyrin complexes and discuss the observed variations in ^{59}Co chemical shifts and line widths in a variety of solvent compositions. Possible hydrogen-bonding effects are discussed, as is the feasibility of using ^{59}Co data to predict ^{57}Fe chemical shifts.

Experimental Section

Materials. Starting compounds for syntheses such as Co(TPP) (Midcentury) and Co(OEP) (Aldrich) were used as obtained. Solvents and CF_3SO_3H were distilled before use. Imidazole (Aldrich) was vacuum sublimed and *N*-methylimidazole (Aldrich) was distilled prior to use.

Preparations. Pentaammine complexes were generally prepared according to the method of Dixon et al.[13] Preparations of cobalt(III) porphyrins with axial ligands normally followed published procedures.[8,14] Perchlorate complexes were converted to the tetraphenylborates by dissolving them along with an excess of $NaBPh_4$ in THF and stirring several hours. The THF was evaporated and the residue washed with water to remove $NaClO_4$ and remaining $NaBPh_4$. The residue was dissolved

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(1) Recipient NIH Research Career Development Award, 1983–1988.

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Table I. Cobalt NMR Data for Pentaammine Complexes

complex	anion	solvent	chem shift, ppm	$\omega_{1/2}$, Hz	ref
$Co(NH_3)_6^{3+}$	*d*	H_2O	8160 ± 73[a,b]	180[c]	*b, c*
$Co(NH_3)_5(N_3)^{2+}$	*d*	H_2O	9100	525	*b*
$Co(NH_3)_5(NO_2)^{2+}$	*a*	*a*	7495 ± 80[a,b]	200	*b*
$Co(NH_3)_5(NCS)^{2+}$	*d*	*d*	8200	*d*	*b*
$Co(NH_3)_5(py)^{3+}$	$CF_3SO_3^-$	CH_3OH	8272	1700	*e*
		Me_2CO	8245	2200	
$Co(NH_3)_5(HIm)^{3+}$	$CF_3SO_3^-$	H_2O	8170	230	*e*
		CH_3OH	8208	350	
$Co(NH_3)_5(CH_3Im)^{3+}$	$CF_3SO_3^-$	H_2O	8178	240	*e*
		CH_3OH	8215	390	
$Co(NH_3)_5(H_2O)^{3+}$	*a*	H_2O	9060[a,b,f]	5000	*b*
	$CF_3SO_3^-$	H_2O	9114	3300	*e*

[a] Average values under variety of conditions (anion, solvent, instruments, etc.) from different laboratories; see note *b*. [b] Reference 2. [c] Reference 27. [d] Unspecified. [e] Data of present study; temperature 24 ± 2 °C. [f] Average recalculated here after deletion of incorrect value in original literature.

Table II. $[Co(por)(RIm)_2]^+X^-$ NMR Data in Methanol[a]

porphyrin	RIm	anion	chem shift, ppm	$\omega_{1/2}$, Hz
TPP	HIm	ClO_4^-	8300	500
TPP	CH_3Im	ClO_4^-	8355	860
TPP	HIm	$B(Ph)_4^-$	8302	700
TPP	CH_3Im	$B(Ph)_4^-$	8354	1000
TPP	HIm	BF_4^-	8300	430
TPP	CH_3Im	BF_4^-	8355	920
OEP	HIm	BF_4^-	8753	130
OEP	CH_3Im	BF_4^-	8810	230

[a] Compound concentration between 2 × 10^{-3} and 4 × 10^{-3} M; temperature 24 ± 2 °C.

Table III. Dependence of ^{59}Co NMR Results on Solvent[a]

RIm	solvent	temp, °C	chem shift, ppm	$\omega_{1/2}$, Hz
HIm	CH_2Cl_2	23.9	8389	1000
CH_3Im	CH_2Cl_2	24.4	8443	1000
HIm	THF	23.7	8392	660
CH_3Im	THF	24.2	8401	1000
HIm	Me_2CO	23.1	8350	330
CH_3Im	Me_2CO	23.3	8409	500
HIm[b]	CH_3OH	22.0	8300	500
CH_3Im[b]	CH_3OH	23.3	8355	860
HIm	$ClCH_2CH_2Cl$	23.6	8360	1600
CH_3Im	$ClCH_2CH_2Cl$	23.8	8392	1600
HIm	CH_3CN	23.6	8345	330
CH_3Im	CH_3CN	23.5	8368	500

[a] All compounds are of the type $[Co(TPP)(RIm)_2]ClO_4$ at about 3 × 10^{-3} M concentration. [b] For results in methanol with other compounds, see Table II.

either in ether (HIm complex) or THF (MeIm complex) and anhydrous Na_2SO_4 added. After the mixture was allowed to stand, the Na_2SO_4 was removed on a Buchner funnel. The HIm complex was purified by recrystallization from ethyl ether and the MeIm complex by repeated washings with ethyl ether.

NMR Spectra. The sample was dissolved in the appropriate solvent and filtered into a 10-mm NMR tube fitted with a coaxial 5-mm tube containing the reference (0.1 M $K_3Co(CN)_6$) in lock solvent D_2O. The spectra were obtained on a Bruker WM 250 at 59.297 MHz. The decoupler was used to maintain tube temperature within 0.5 °C; the temperature was recorded on a Doric 410A digital thermometer. The collected FID's were exponentially multiplied before being Fourier transformed. Typically about 12000 scans were required to obtain a good signal-to-noise ratio for a porphyrin complex.

Results

General Considerations. The chemical shifts δ and line widths $\omega_{1/2}$ (full width at half-height) of cobalt(III) complexes (both with and without porphyrin rings) were measured. In Table I the NMR data for pentaammine complexes of interest are presented, and in Table II data are given for a variety of $[Co(por)(RIm)_2]X$ compounds in methanol. Abbreviations are as follows: por = porphyrin dianion; RIm = imidazole (HIm) or *N*-methylimidazole (MeIm); $X^- = CF_3SO_3^-, ClO_4^-, BPh_4^-$, or BF_4^-. Results in six solvents are given for two types of porphyrin rings, tetraphenylporphyrin (TPP) and octaethylporphyrin (OEP). From repeat experiments on separate samples and days, we estimate that the chemical shifts δ are reproducible to 2 ppm. The line widths are reproducible to about 10% of their value.

Pentaammine Complexes. In order to compare the influence of imidazoles and related nitrogen ligands to that of ammonia, experiments on a number of pentaammine complexes were carried out. Results are in Table I. The δ values for the HIm and MeIm complexes are very close to that of the hexaammine, and there is a small but significant difference between the two imidazole compounds. Comparisons with data for five other ligands are included in Table I.

Porphyrin Complexes. In order to determine how the chemical shift in one solvent depends on the components of $[Co(por)(RIm)_2]X$, the data in Table II were obtained. The porphyrin rings TPP and OEP were chosen because hydrogen bonding to substituents on the porphyrin periphery is not possible, so that any effects seen must involve an interaction between the solvent and the axial imidazole ligands.

It can be seen in Table II that the chemical shift in methanol is independent of the nature of the anion. Since methanol has a fairly large dielectric constant and the cobalt porphyrin concentration is quite low (ca. 10^{-3} M), ion-pairing effects may not exist and δ would then be constant. In solvents of lower dielectric constant, we have observed small anion effects (ca. 10 ppm); these will be discussed in a later communication.

Changing the axial ligand from HIm to MeIm causes δ to increase by 56 ± 1 ppm in methanol. The nature of the porphyrin has an important influence; for both imidazoles the OEP derivatives have a higher δ than the TPP ones by 454 ± 1 ppm. This change is large enough to indicate that a study of ^{59}Co NMR in complexes of the natural porphyrins would be worthwhile.

It is well-known that the ^{59}Co chemical shift is dependent on solvent nature. This is of particular interest here because the hydrogen-bonding properties of cobalt-bound HIm would be different from those of cobalt-bound MeIm. This would, of course, be relevant to the suggested importance of hydrogen bonding to/from the histidines in heme proteins. Data for complexes $[Co(TPP)(RIm)_2]ClO_4$ in six solvents are given in Table III. Most of the differences therein in δ and $\omega_{1/2}$ are well outside experimental error; to a degree, these will be discussed below. It is noteworthy that in every solvent the MeIm complex has a higher chemical shift than the HIm complex; the differences range from 9 ppm in THF to 59 ppm in acetone. Further possible evidence for solvent hydrogen bonding and/or ion pairing can be seen in Figure 1, which shows chemical shifts for both $[Co(TPP)(HIm)_2]ClO_4$ and $[Co(TPP)(MeIm)_2]ClO_4$ in the mixed-solvent CH_2Cl_2/THF series at two temperatures. An interpretation is given below for the difference in the shapes of the curves of δ vs. solvent composition for the HIm and MeIm complexes. Several other mixed-solvent systems were studied; in all cases the curves for the HIm and MeIm complexes were different, but only in that of Figure 1 was the difference so pronounced.

It is seen in Figure 1 that temperature has an effect on the value of δ; for both complexes the temperature dependence is ca. 1.5 ppm K^{-1}. This is similar in magnitude to what has been found previously[2] with other cobalt(III) complexes. It is clear that in

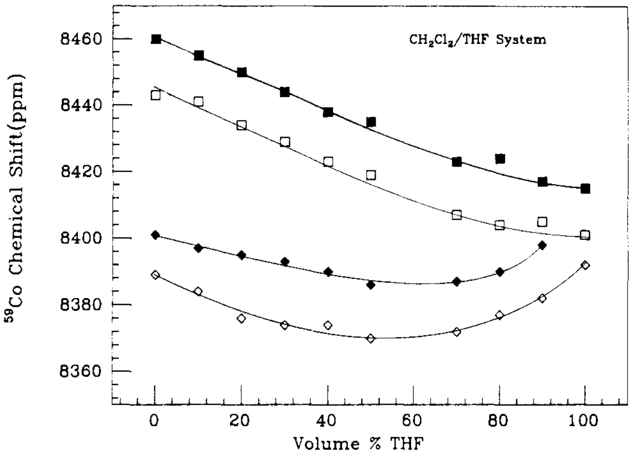


Figure 1. ^{59}Co chemical shifts for $[Co(TPP)(RIm)_2]ClO_4$ in solvent mixtures of CH_2Cl_2 and THF: (◇) R = H and T = 23.9 °C; (◆) R = H and T = 31.5 °C; (□) R = Me and T = 24.2 °C; (■) R = Me and T = 32.7 °C. Percentage solvent is by volume.

order to obtain reliable ^{59}Co NMR data (both δ and $\omega_{1/2}$) good temperature control is essential.

The two complexes were also investigated in CH_3OD, in which the NH hydrogen in the HIm complex would be fairly rapidly deuterated. After a suitable time (several hours), it was found that the δ value had not changed from that in CH_3OH.

Discussion

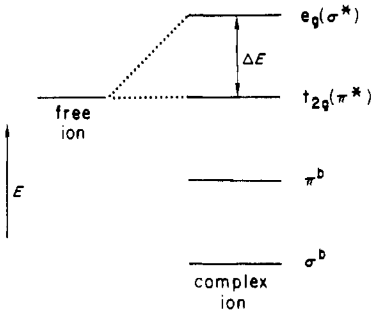
Chemical Shifts. Prior to discussing our results, a few general comments are in order concerning the different magnetic and structure/electronic effects that can influence ^{59}Co shifts. It is well established that the major factor in determining the cobalt chemical shifts is temperature-independent paramagnetism (TIP) arising from the d–d splitting in the ligand field. The most important excited state to contribute to TIP is $^1T_{1g}$, which differs from the ground state ($^1A_{1g}$) according to the configurational change $t_{2g}{}^6e_g{}^0 \rightarrow t_{2g}{}^5e_g{}^1$ in octahedral symmetry. This brings about, for example, a difference in δ of over 12 000 ppm between $Co(CN)_6{}^{3-}$ and $Co(acac)_3$.[2] For complexes of the CoN_6 type the known range is about 3500 ppm.

The ring-current effects that are reported in the literature range up to about 20 ppm in ^{1}H NMR. For example, porphyrin ring currents influence the proton shift on coordinated axial imidazoles by up to 10 ppm. The review by Haigh and Mallion[15] suggests that such effects will be even less with heavier atoms. It seems probable that the change in ^{59}Co δ due to this interaction will be of much smaller magnitude than the TIP influence.

Excitations other than the d–d type can cause paramagnetic chemical shifts, so it is necessary to consider the well-known Q and B bands of the porphyrin system in terms of how they involve the central cobalt. It is found that the placement of the porphyrin bands are little affected by the metal orbitals; the main change caused by the metal is due to its electron-withdrawing power as measured by, for example, electronegativity.[16,17] Theoretical treatments also suggest that the porphyrin excitations are of the $\pi \rightarrow \pi^*$ type. (It is suggested that the cobalt(III) porphyrins may have d–d transitions in the region of the lowest energy $^1Q(\pi,\pi^*)$ transitions.[18,19]) It appears, therefore, that the porphyrin excitations may not significantly influence the position of the cobalt chemical shift.

The position of the first cobalt(III) d–d band is a function of the spectrochemical series, while the δ value depends on both spectrochemical and nephelauxetic series.[20,21] Since we are dealing exclusively with CoN_6 type complexes, for which the nephelauxetic factor will be constant, we can safely discuss changes in terms of an apparent magnetochemical order.

Scheme I



We found that the two quantities obtained for each system—the values of δ and $\omega_{1/2}$—are complementary and together give a coherent picture. It is convenient to discuss them individually, and in this part the results obtained from the δ measurements are explained. In Table I the salient fact seen in the δ values of $Co(NH_3)_6{}^{3+}$, $Co(NH_3)_5(HIm)^{3+}$, and $Co(NH_3)_5(MeIm)^{3+}$ is their close similarity. The conclusion is that the two imidazoles are very close to ammonia in the spectrochemical series, and this is verified by the fact that the wavelengths of the lowest energy d–d bands for these three complexes are the same[22] within experimental error. Further evidence for this is seen in the line widths (vide infra). Since ammonia is only a σ donor while imidazoles can act as σ donors, π acceptors and π donors, it is not clear why they are similar in this series.

Although the δ values for $[Co(NH_3)_5L]^{3+}$ (L = NH_3, HIm, MeIm, py) are close, the differences are real and can be used to place these ligands in a spectrochemical series even though the lowest energy d–d optical transitions are identical in energy (472 ± 1 nm[22]) in all four complexes. Using all of the data in Table I gives the following spectrochemical series: $NO_2^- > NH_3 >$ HIm $>$ MeIm $> NCS^- >$ py $> N_3^-$. *We conclude that ^{59}Co NMR may be more sensitive than optical spectroscopy for placing ligands in the spectrochemical series.* A corollary to this is the possibility that ^{59}Co chemical shifts can be used to determine d–d transition energies when they are obscured by other more intense (allowed) bands, as in metalloporphyrins.

A second salient fact (from Tables I–III) is that the chemical shift for complexes with MeIm is higher (more deshielded) than those with HIm. The more electron-releasing ligand (MeIm) moves δ to higher values. One motive for our study was to discern if the ^{59}Co chemical shift in a porphyrin complex with axial ligands would show a movement with solvent nature that could be attributed to hydrogen bonding to the N–H hydrogen of HIm. In order to correct for other solvent effects, direct comparisons of $Co(por)(RIm)_2{}^+$ (R = H, Me) were made. Although the MeIm complex always has a higher δ, the difference between R = H and R = Me is not constant with solvent. Interpretation is not easy, with the possible exception of the CH_2Cl_2 and THF series shown in Figure 1. The *relative* change of δ for $Co(TPP)(HIm)_2{}^+$ toward higher δ in THF can be interpreted in the same fashion as for the change from R = H to R = Me. Hydrogen bonding of oxygen on THF to the N–H hydrogen on imidazole should cause an electron shift toward the metal. If this is transmitted by the π system (vide infra), the cobalt should be more deshielded as observed.

The change from TPP to OEP is in the direction of strong electron release to the cobalt. Phenyl groups when noncoplanar are electron-withdrawing and ethyl groups are electron-releasing. Assuming that the porphyrin π orbitals interact with the d_{xz} and d_{yz} orbitals of cobalt, the direction of movement of δ on change from $Co(TPP)(RIm)_2{}^+$ to $Co(OEP)(RIm)_2{}^+$ again indicates higher δ correlates with greater electron release.

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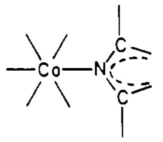
According to the Ramsey equation (vide infra) the δ values for cobalt(III) compounds are dominated by an inverse correlation with $\Delta E(^1A_{1g} \rightarrow {}^1T_{1g})$, where ΔE approximates to the separation between the t_{2g} and e_g orbitals. We now ask how electron release by a ligand substituent will influence ΔE and therefore δ.

Imidazole ligands can donate electrons to metals either through the σ framework or through the π bonds. We use arguments akin to those of McClure,[23] where the d orbitals are divided up into σ and π levels as shown in Scheme I. Both π^b and σ^b are occupied ligand-based orbitals. If the change in electron release of the imidazole ligand is primarily transmitted via the σ bonds, the σ^* molecular orbitals will be raised. Therefore the value of ΔE is increased and δ is lowered; this is opposite in direction to what is observed when R = H is converted into R = Me. On the other hand, if the change in electron density is transmitted via the π bonds, the π^* level is raised and ΔE reduced, with a consequent increase in δ. Electronic influences fall off rapidly on transmission through a σ framework, but such a falloff is less serious for transmission through a π framework. Thus, it is not surprising that the remote R group in RIm can exert its electronic effect upon the π orbitals of the cobalt atom. Support for the π-transmission conclusion is obtained from the recent literature in which the electronic interactions of imidazole ligands with the metal have been studied. Relevant observations have been made on proton NMR of low-spin ferric porphyrin complexes,[24] hydrogen bonding to methoxide in an iron porphyrin,[25] and ionization and NMR shifts of bound imidazole ligands in octahedral complexes.[22]

The above energy level argument was made for imidazole ligands. It is, of course, equally applicable to the porphyrin ligands studied here. After our work was complete, we found that a similar rationalization for some ^{55}Mn chemical shifts had been made.[26]

The chemical shifts of simple CoN_6 type complexes vary considerably as may be seen in Table I and in the literature.[2] Therefore it was somewhat surprising when the shifts for our porphyrin complexes fell near to that of $Co(NH_3)_6^{3+}$ (Tables I–III). Because of the intense porphyrin transitions in the same spectral region where CoN_6 compounds have their d–d transitions, the d–d bands for cobalt(III) porphyrins with axial ligands have not yet been uncovered. Therefore, using these bands to predict δ values for the porphyrin complexes was not possible. Nevertheless, the raw conclusion from the similarity of δ values for $Co(NH_3)_6^{3+}$ and $Co(TPP)(HIm)_2^+$ is that each nitrogen of the porphyrin ring (as well as the imidazole ring (vide supra)) has a spectrochemical position like that of ammonia. Unlikely as this may sound, the facts (including line widths (vide infra)) all are consistent with this conclusion. The local environment about a cobalt–nitrogen link, whether the nitrogen ligand be imidazole or porphyrin, is



Since imidazole is placed near ammonia in the spectrochemical series, both by ^{59}Co NMR (Table I) and by d–d transitions, we conclude that this type of local environment in porphyrins also should be similar to that of ammonia. It is inherent in this conclusion that the chemical shift anisotropy in complexes of the type $Co(por)(RIm)_2^+$ should be quite small.

Line Widths. Because of its quadrupole moment, the cobalt will couple with the electric field gradient at the nucleus. A number of relaxation mechanisms can be considered for the porphyrin complexes with axial ligands. Chemical-exchange mechanisms are unlikely in the time frame of the NMR experiments, and dipolar broadening should not be a problem at these low concentrations (ca. 10^{-3} M). Ligand nitrogen–cobalt scalar coupling such as occurs in $Co(NO_2)_6^{3-}$ and $Co(NH_3)_6^{3+}$ is estimated to be about 50 Hz;[4] the observed line width for $Co(NH_3)_6^{3+}$ is 183 ± 10 Hz at 5.872 T.[27] Some of the complexes studied herein have line widths of this magnitude.

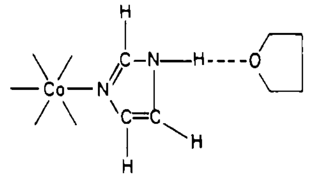
Correlation times for the cobalt porphyrin complexes should follow eq 1 provided the line width is not field-dependent. The

$$\frac{1}{T_2} = \frac{3}{40}\left(\frac{e^2qQ}{\hbar}\right)^2\left(1 + \frac{\eta^2}{3}\right)\left\{\frac{2I+3}{I^2(2I+1)}\right\}\tau_c \qquad (1)$$

symbols in eq 1 have their usual meaning, with η being the asymmetry parameter. Although a detailed treatment of this equation is not presently possible, some aspects are already clear. In the rotational correlation time τ_c the bulk viscosity should appear. Values of $\omega_{1/2}$ for the porphyrin complexes given in Table III show the following solvent order: $ClCH_2CH_2Cl > CH_2Cl_2 > THF > MeOH > Me_2CO \approx MeCN$. Literature values for solvent viscosity place this order as $ClCH_2CH_2Cl > MeOH > CH_2Cl_2 > MeCN > Me_2CO$. The line widths are roughly correlated with viscosity; molecular tumbling times are therefore important, but solvent and compound structure also play a role.

The line widths for OEP complexes are only about one-third of those for TPP complexes. Although the reason for this is not presently clear, a significant advantage to the use of OEP in future studies (e.g., of $\omega_{1/2}$ as a function of field strength) is visualized.

Except for the two chlorocarbon solvents, which have large $\omega_{1/2}$ values, the values of $\omega_{1/2}$ are smaller for the HIm complexes than for the MeIm analogues for both the porphyrin and pentaammine complexes. Inherent in these observations is the implication that hydrogen bonding is playing a role in a manner not simply related to size. This can be seen from the following facts. In the chlorocarbon solvents the line widths for $Co(TPP)(HIm)_2^+$ and $Co(TPP)(MeIm)_2^+$ are the same and are moderately large, albeit much smaller than for the structurally similar *trans*-$Co(en)_2Cl_2^+$ in many solvents. Addition to CH_2Cl_2 of a cosolvent such as THF that can interact with the HIm complex in the manner



causes a decrease in line width, but there is no change for the MeIm analogue. In the mixed solvent $CH_2Cl_2/MeOH$ the $\omega_{1/2}$ value for $[Co(TPP)(HIm)_2]BF_4$ decreases monotonically with increasing fraction of MeOH from 920 ± 50 to 430 ± 20 Hz while the $\omega_{1/2}$ value for the MeIm analogue remains constant at 920 ± 50 Hz. In a related experiment, it was found that small amounts of phenanthroline (which can hydrogen bond to cobalt-bound HIm but not replace it[8]) causes a marked reduction in $\omega_{1/2}$ for $[Co(TPP)(HIm)_2]BF_4$ in CH_2Cl_2.

The increase in compound size on forming the hydrogen bond to THF, MeOH, and phen must have been more than compensated for in the other line-width-determining factors in eq 1. There are two that do not remain constant as the ligand changes, specifically q and η, both of which increase as the electric field asymmetry increases. If hydrogen bonding modifies the crystal field splitting ability of imidazole in such a way as to make this ligand more equivalent to the nitrogens of the porphyrin ring, both q and η will decrease, causing $1/T_2$ and $\omega_{1/2}$ to decrease as observed.

On the basis of a comparison of the chemical shifts of $Co(NH_3)_6^{3+}$, $Co(NH_3)_5(RIm)^{3+}$, and $Co(por)(RIm)_2^+$ we concluded that the nitrogen ligands (RIm, NH_3, por) have similar positions in the spectrochemical series and that the chemical shift anisotropy in $Co(por)(RIm)_2^+$ is relatively small. On the basis of the fact

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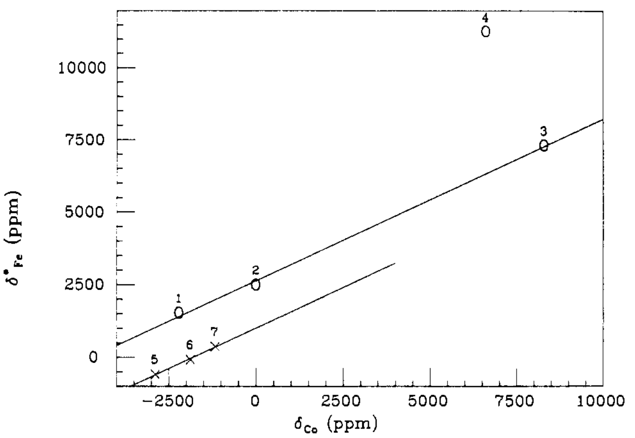

Figure 2. Correlation of ^{57}Fe chemical shifts (relative to $Fe(CO)_5$)) with ^{59}Co chemical shifts (relative to $K_3Co(CN)_6$). The numbers in the plot refer to the following compounds (with literature reference): (1) $Fe(C_5H_5)_2$[31] and $Co(C_5H_5)_2^+$;[32] (2) $Fe(CN)_6^{4-}$[31] and $Co(CN)_6^{3-}$ ($\delta = 0$); (3) $Fe(TPP)(py)_2$[33] and $Co(TPP)(HIm)_2^+$ (this study); (4) $Fe(bpy)_3^{2+}$[34] and $Co(bpy)_3^{3+}$;[2] (5) $(cbd)Fe(CO)_3$[31] and $(cbd)Co(C_5H_5)$[35] (cbd = cyclobutadiene); (6) $(chd)Fe(CO)_3$[31] and $(chd)Co(C_5H_5)$[35] (chd = cyclohexadiene); (7) $(cod)Fe(CO)_3$[31] and $(cod)Co(C_5H_5)$[35] (cod = cyclooctadiene). The slopes of both lines have the value 0.57.

that the $Co(OEP)(RIm)_2^+$ cations have line widths very similar to that of $Co(NH_3)_6^{3+}$ (where q and η are effectively zero), we arrive at the same conclusion. In view of the importance of chemical shift anisotropy in ^{59}Co and ^{57}Fe NMR[28-30] and the possibility of calculating d–d band positions for the cobalt and iron porphyrins if the spectrochemical conclusion is correct, we plan to investigate the dependence of line width on magnetic field strength.

Correlation of ^{57}Fe and ^{59}Co Chemical Shifts. Because of the difficulty in obtaining chemical shift values for iron complexes, it was our hope that the cobalt data could be used to predict ^{57}Fe shifts for the analogous iron compounds. If, as is usually the case, the TIP contribution to the chemical shift is dominated by a single excitation for d^6 low-spin complexes, the Ramsey equation can be written according to eq 2, in which "A" is a constant incorporating the reference and ΔE is the energy of the relevant d–d excitation.

$$\delta = A + B/\Delta E \qquad (2)$$

To a good approximation[20] the "B" term includes a collection of constants multiplied by the expectation value of r^{-3} for the electrons in the 3d shell, $\langle r_{3d}^{-3}\rangle$. A plot of δ vs. $1/\Delta E$ gives a good linear correlation for octahedral cobalt(III) complexes with ligands of the first period. The B term is a constant when the ligands are all from the first period (C, N, O, F). When ligands from the other periods are included, the B term varies somewhat due to the nephelauxetic effect ($\langle r_{3d}^{-3}\rangle$); however, a correction can be applied[20,21] such that the plot δ vs. $1/\Delta E$ is linear for all ligand types. For the complexes reported herein, all the ligands are from the first period and a nephelauxetic effect correction is not needed.

Table IV. Chemical Shifts for Oxothioanions[a]

anion[b]	^{51}V, ppm[c]	^{95}Mo, ppm	anion[b]	^{51}V, ppm[c]	^{95}Mo, ppm
MO_4^{n-}	0[c]	0	MOS_3^{n-}	1280	1655
MO_3S^{n-}	290	498	MS_4^{n-}	1940	2260
$MO_2S_2^{n-}$	720	1068			

[a] In D_2O at 24 ± 2 °C. [b] For vanadates, $n = 3$; for molybdates, $n = 2$. [c] To convert to the $VOCl_3$ standard, subtract 541 ppm from these values.

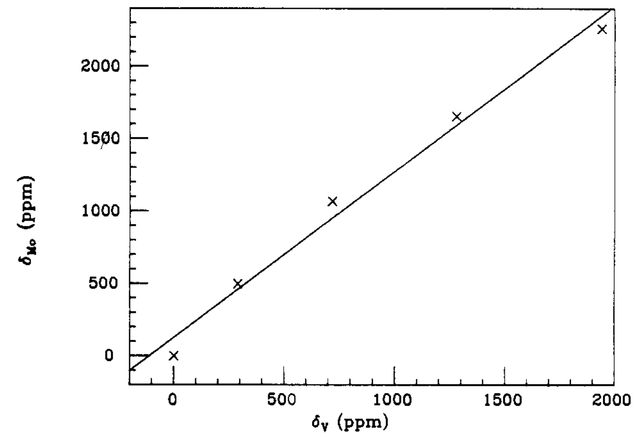

Figure 3. Correlation of ^{95}Mo chemical shifts for oxothiomolybdates $MoO_{4-x}S_x^{2-}$ with ^{51}V chemical shifts for the corresponding oxothiovanadates. Chemical shifts increase with x for both metals. The shifts are relative to the oxoanions MoO_4^{2-} and VO_4^{3-}.

In analogy with cobalt(III), one can write eq 3 for iron(II) complexes. For octahedral cobalt(III) and iron(II) complexes

$$\delta^* = A^* + B^*/\Delta E^* \qquad (3)$$

$$\delta^* = m\delta + \text{constant} \qquad (4)$$

it is reasonable to assume that changes in B will parallel those in B^* and that ΔE will parallel ΔE^* when a change in ligand occurs. It then follows that δ and δ^* are linearly related (eq 4). Actually, to obtain a linear equation, it is sufficient that the ratio $B/\Delta E$ parallels $B^*/\Delta E^*$. With use of ^{57}Fe chemical shifts available from the literature,[31-35] a plot of δ^* vs. δ for analogous iron and cobalt complexes was constructed and is shown as Figure 2. The three points defined by $Fe(C_5H_5)_2/Co(C_5H_5)_2^+$, $Fe(CN)_6^{4-}/Co(CN)_6^{3-}$, and $Fe(TPP)(py)_2/Co(TPP)(HIm)_2^+$ are shown as circles and form a line of slope $m = 0.57$. (The point for $Fe(TPP)(py)_2/Co(TPP)(HIm)_2^+$ is valid because py and HIm are nearly identical in the spectrochemical series.) Interestingly, the point for $Fe(bpy)_3^{2+}/Co(bpy)_3^{3+}$ is far off the correlation line. This, however, is expected because $Fe(bpy)_3^{2+}$ has a low-energy M → L charge-transfer excitation (in addition to the usual d–d excitation) that contributes to the chemical shift. Note that the deviation of δ^* for $Fe(bpy)_3^{2+}$ is in the expected direction.

The three points defined by crosses refer to the d^8 couples $(diene)Fe(CO)_3/(diene)Co(C_5H_5)$, in which the diene is varied.[31,35] The line formed by these couples does not coincide with the main one at least in part because the $(CO)_3^0$ moiety differs from the $C_5H_5^-$ moiety. Note, however, that the slope of this line is the same as for the main line, indicating that only a single correction for the moiety difference is needed; i.e., the shiftability is independent of oxidation state.

From the correlations observed it is clear that the iron and cobalt chemical shifts for a variety of compounds are related in an extremely simple way. Therefore, the assumption that changes in $B/\Delta E$ and $B^*/\Delta E^*$ are parallel is justified. One can expect that the other low-spin d^6 complexes (e.g., Mn(I), Ru(II), Pt(IV), etc.) can be similarly correlated.[36] On the basis of the results with the d^8 diene complexes, the same may also be true of low-spin d^8 complexes.

It is fair to ask if supporting evidence of an independent nature is available. There are some metal chemical shifts for vanadium and molybdenum oxothioanions that provide a test.[37] These data,

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given in Table IV, are for d^0 complexes where excitation is of the charge-transfer type. In Figure 3 a plot of $\delta(VO_{4-x}S_x^{3-})$ vs. $\delta(MoO_{4-x}S_x^{2-})$ is given, and again an excellent correlation is evident. The relative shiftability yielded by the data is 1.16 for Mo/V. A similar correlation for $^{183}W/^{95}Mo$ oxothio compounds has been reported.[38]

It is also fair to ask what limitations are expected for correlations of this type. There are several. (1) Elements of low atomic number having no low-energy excitations of appropriate transition type will require treatment by the full Ramsey equation. (2) Whenever a compound has an unusual excitation (e.g., $Fe(bpy)_3^{2+}$), there should be a marked deviation from the correlation line; this type of deviation can be useful in predicting excitation symmetries. (3) The influences of medium and charge have been ignored; for the cases herein where $\Delta\delta$ is large this is not a problem, but when $\Delta\delta$ values are small it could influence the degree of correlation.

If the $^{57}Fe/^{59}Co$ chemical shift correlation proves valid, it will allow the prediction of shifts in iron complexes. This should be especially interesting,[39,40] although it has yet to be established that ^{59}Co NMR of cobalt-substituted proteins can be obtained without excessively broad lines (due to slow tumbling and the nuclear quadrupole moment).

Acknowledgment. This work was supported by grants from the National Institutes of Health (Grant No. AM 30145 and AM 01151 and the BRSG Fund of Brown University). We are grateful to Drs. P. J. Domaille and J. G. Jones for helpful discussions, to Dr. J. Van Epp for technical assistance, and to Professor R. G. Kidd for useful suggestions.

Registry No. ^{59}Co, 7440-48-4; ^{57}Fe, 14762-69-7; $[Co(NH_3)_5(py)]\cdot 3CF_3SO_3$, 100447-66-3; $[Co(NH_3)_5(HIm)]\cdot 3CF_3SO_3$, 100447-67-4; $[Co(NH_3)_5(CH_3Im)]\cdot 3CF_3SO_3$, 100466-08-8; $[Co(NH_3)_5(H_2O)]\cdot 3CF_3SO_3$, 69897-22-9; $[Co(TPP)(HIm)]\cdot ClO_4$, 41136-67-8; $[Co(TPP)(CH_3Im)]\cdot ClO_4$, 100447-68-5; $[Co(TPP)(HIm)]\cdot B(Ph)_4$, 100569-86-6; $[Co(TPP)(CH_3Im)]\cdot B(Ph)_4$, 100569-09-3; $[Co(TPP)(HIm)]\cdot BF_4$, 69531-88-0; $[Co(TPP)(CH_3Im)]\cdot BF_4$, 69531-90-4; $[Co(OEP)(HIm)]\cdot BF_4$, 100466-10-2; $[Co(OEP)(CH_3Im)]\cdot BF_4$, 100466-11-3.

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Contribution from the Department of Chemistry,
Brandeis University, Waltham, Massachusetts 02254

Structure, Reactivity, and Electrochemistry of Free-Base β-Oxoporphyrins and Metallo-β-oxoporphyrins

Alan M. Stolzenberg,* Paul A. Glazer, and Bruce M. Foxman

Received September 17, 1985

The free-base and metal complexes of mono- and di-β-oxoporphyrins obtained by hydrogen peroxide oxidation of octaethylporphyrin have been prepared and certain chemical and physicochemical properties investigated. One of these complexes, which are formally analogous to hydroporphyrins, has been proposed to be the essential chromophoric unit of the macrocycle in heme-d_1. The structure of [3,3,7,8,12,13,17,18-octaethyl-2(3*H*)-porphinonato(2−)]nickel, $C_{36}H_{44}N_4ONi$, has been determined by X-ray diffraction. The complex crystallizes in the monoclinic space group *C*2/*c* with $a = 38.565$ (8) Å, $b = 14.767$ (4) Å, $c = 17.327$ (5) Å, and $\beta = 102.19$ (3)°. There are 12 molecules of the oxoporphyrin per unit cell including four disordered molecules on a special position. The structure has been refined by full-matrix least squares to $R = 0.106$. The results confirm the structure of the oxoporphyrin macrocycle previously deduced by spectroscopic evidence. The conformations of the two independent molecules are different. The general position molecule is nearly planar, whereas the special position molecule is S_4 ruffled. Both deviate from planarity to a lesser extent than nickel hydroporphyrin complexes. The β-carbonyl group of oxoporphyrins has been found to be remarkably inert. The electrochemical properties of oxoporphyrins are unlike those of hydroporphyrins. The first oxidations of mono- and dioxoporphyrins occur at potentials quite similar to that of octaethylporphyrin. In contrast, the potentials of the first reductions become successively less negative as more carbonyl groups are introduced.

Introduction

The oxidation of octaalkylporphyrins with hydrogen peroxide in acidic media was first investigated by Fisher in the 1930s.[1] The main product had a UV–vis spectrum that resembled those of chlorins and was initially assigned a β,β′-dihydroxychlorin structure, but later studies established that it contained only one oxygen atom.[2] The correct *gem*-dialkyl-β-oxoporphyrin[3] structure was not assigned until 1964.[4,5] The reaction was interpreted as an acid-catalyzed pinacol–pinacolone rearrangement of an initially formed β,β′-dihydroxychlorin,[4,6] a view confirmed by the sulfuric acid-catalyzed rearrangement to identical materials of porphyrins oxidized by OsO_4.[2,4] Later thorough reexaminations of the peroxide reaction system established that reaction did not halt at the mono-β-oxoporphyrin stage.[6-8] All possible isomeric dioxoporphyrin and several isomeric trioxoporphyrins have been isolated from the oxidation of octaethylporphyrin.[8] Structures of octaethylmonooxoporphyrins and -dioxoporphyrins, **5–10**,[9] are depicted in Chart I.

The structure, physical properties, and reactivity of free-base and metallo-β-oxoporphyrins have not been investigated exten-

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