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Electron Spin Resonance and Electronic Structure of Vanadyl−Porphyrin in Heavy Crude Oils

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A study of vanadyl−porphyrin by electron spin resonance (ESR) was carried out looking for answers about the role that the central V═O ion plays when these kinds of molecules are present in heavy crude oils. The eigenvalues of the linear combination of atomic orbitals (LCAO) were obtained from the experimental values of *g* and parameters (ESR). The contributions to the molecular orbitals that describe the various energy levels of vanadyl ion were also obtained for the porphyrin species. The trends of the degree of covalent character of the metal−ligand bonds and the length of the vanadium−oxygen chemical bond are discussed. It is interesting to note that the Fermi contact term, K_{eff}, is essentially constant for all samples investigated, and it was found to be independent of the calculated electron delocalization $(1 - \delta^2)$ and shows only little variation among the three different samples of oil. The orbital energies derived from our ESR study qualitatively agree with those predicted from MO theory for synthetic vanadyl−porphyrins.

Introduction

The existence of trace metals in crude oil has been studied for a long time,[1] and the presence of these species in the different steps of oil processing has had a negative influence because they can act as dopants of the catalyst systems.[2] Traces amounts of several metals are often found, but nickel and vanadium have been characterized as the dominant species and in particular vanadium as the most important dopant.[3] The most common occurrence of vanadium in these fossil samples is in the form of vanadyl−porphyrinate.[4] Although previous ESR studies have shown that vanadium is present in crude oils mainly as metalloporphyrin type compounds, little work[5,6] has been carried out to study carefully separated and analyzed vanadyl−porphyrin pure fractions obtained from heavy crude oil samples by ESR spectroscopy. Furthermore, some studies using other spectroscopic techniques[7,8] that have been very useful to show the structural characteristics of these derivatives have been performed. There is also a very interesting theoretical work[9] in which the ESR **g** tensors are obtained and compared with the experimental values.

Our mass spectrometry[10,11] study shows that the vanadyl ion is predominately present as a pure major fraction of isolated and purified vanadyl porphyrins from some heavy crude oil samples. It is present as two major homologous series, namely, etioporphyrin (Etio) and deoxophylloerithroaetio (DPEP), and three minor homologous series, tetrabenzoporphyrin (THBD), benzoporphyrin (B), and benzoporphyrin-DPEP (BD) structures.[12,13]

Taking advantage of the high purity of our samples and knowing the complexity of the pure fraction of the petroporphyrins, we demonstrate that the vanadyl−oxygen bond is distorted. This result is qualitatively derived from the different structure types, and their complexity depends on the nature of these compounds in heavy crude (with respect to the maturity of the crude oil samples). The present work is based on a spectroscopic study (EPR) which yields information of the coordination geometry of the vanadyl ion bond in natural petroporphyrins. This kind of study is useful to get a quantitative measure of the V═O bond strength, as well as the average of the degree of covalent character of the V═O bonds and the degree of distortion of the V═O bond in porphyrin macrocycles. This topic also has an influence on the electron delocalization and its influence on the Fermi contact term.

Experimental Section

The heavy crude oils used in this study were obtained from Pémex, the Mexican government owned oil company. Conventional silica and alumina column chromatography and successive purifications by thin-layer chromatography (TLC) were used to obtain pure vanadyl

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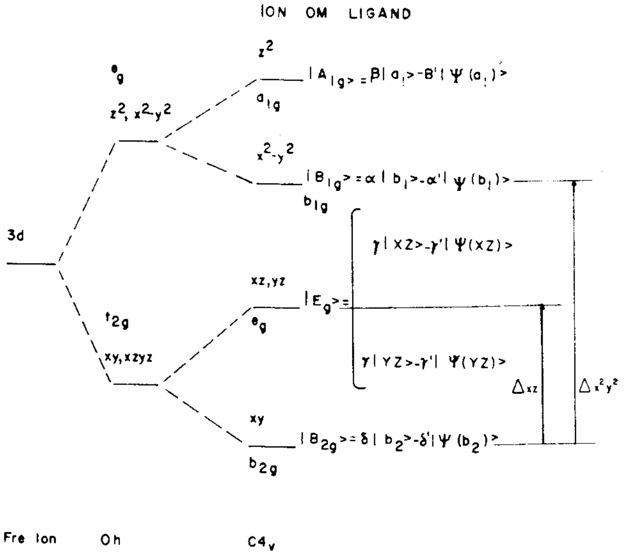
Table 1. ESR Parameters of Isolated Vanadyl−Porphyrins[a] in Heavy Crude Oils

sample	$g_\perp$	$g_\parallel$	$A_\perp$	$A_\parallel$	K_{eff}	contrib from pyrrole $A_\parallel$
VO Ixtal-101	1.9862	1.9629	55	157	0.52	7.0
VO Zaap-1	1.9935	1.9697	48	145	0.50	5.0
VO Ceeh-1	1.9929	1.9712	51	144	0.50	6.0
VO TBP[b]	1.985	1.962	50	150	0.50	7.0
VO Etio[c]	1.9862	1.9629	60	157	0.53	7.0

[a] Energy units: 10^{-4} cm^{-1}. [b] References 19 and 20. [c] References 20 and 21.

Scheme 1. Energy Levels to Ion Metallic of Transition 3d to Field of Octahedric Symmetry C_{4v}[a]



[a] The splitting ΔE_{xz} is a measure of distortion, whereas $\Delta E_{x^2-y^2}$ shows no dependence on distortion.

porphyrins. The visible−ultraviolet spectra of the vanadyl porphyrins were obtained using a Perkin-Elmer Lambda 5 spectrometer. The samples were scanned in the range 350−700 nm. The characteristic Soret band located at 402 nm and two minor bands, namely, α at 532 and β at 572 nm, were well identified. The mass spectrometry was performed in a Finnigan Mat TSQ-70 spectrometer by direct introduction and electron impact (MS-EI). The ESR measurements were carried out in a Bruker 200-SCR-AD X-band spectrometer with 100 kHz modulation at 76 K. The microwave frequency was 9.5 GHz.

Interpretation of the ESR Spectra. Shoulders in the ESR spectrum at magnetic field values corresponding to $g_\parallel$, with multiple splitting due to the hyperfine coupling tensor component $A_\parallel$, can be seen. Similarly the magnetic field values corresponding to $g_\perp$ were found to have an eight-line multiple pattern due to $A_\parallel$. The measured parameters are given in Table 1.

Molecular orbital theory was used to relate the measured principal components of the **g** and **A** tensors to changes in the geometry and the electronic structure of vanadyl species. The splitting of the orbitals in transition-metal ions in octahedral and distorted ligand fields has been considered by other authors.[12−18]

Our experimental observations show (see Table 1) that $g_\parallel > g_\perp$ in the electronic ground state indicating a tetragonal distortion.

For simplicity we assume that the molecule of the vanadyl porphyrins contained in the crude oil resins approximately belongs to the C_{4v} group of symmetry, as is shown in Scheme 1.

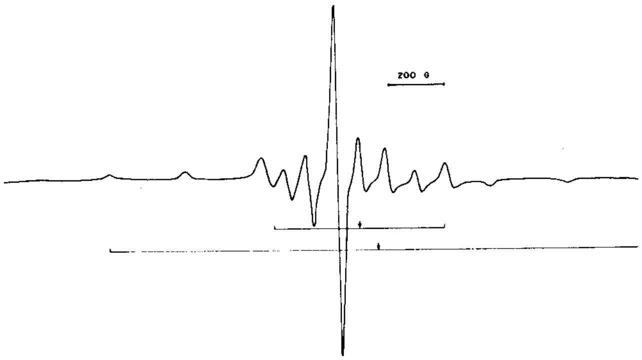


Figure 1. Typical ESR spectra of V═O in porphyrins correspond to ESR signals of V^{4+}.

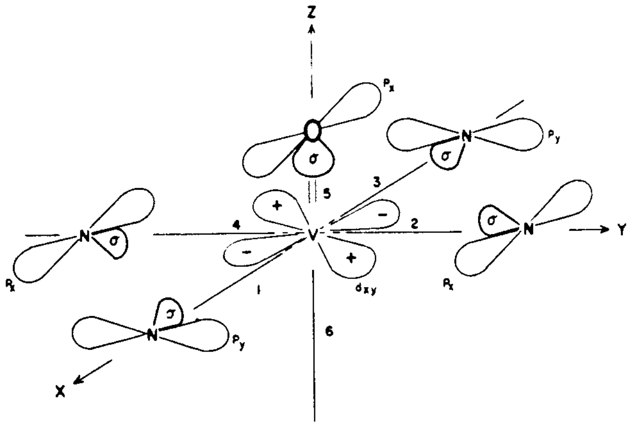


Figure 2. Molecular structure of ion VO^{2+} in porphyrins. The average symmetry corresponds to C_{4v} where the nitrogen ligands 1−4 form a square parallel to the surface.

The normal surface defines the distinguished axis (z). The bond between oxygen atom 5 and the vanadium atom, which corresponds to the $V{=}O^{2+}$ double bond, is considerably shorter than the bond to nitrogen atoms 1−4. This set forms a square, parallel to the plane of the surface (Figure 2).

We briefly review the information about the tetragonal distortion and electron delocalization from ESR parameters. For this purpose the notation[14] of molecular orbitals is defined. Each ligand contributes to a filled σ type orbital directed along the bond to the vanadium ion, and, furthermore, there are two filled p orbitals in a perpendicular position to that direction (see Scheme 1). On the central vanadium atom the 3d and 4s orbitals are considered.

The bonding molecular orbitals are mainly centered on the ligands and are filled by electrons from the organic fragment. The antibonding linear combinations are predominantly centered on the vanadium ion. The most relevant orbitals[14] for the present discussion are listed in order of increasing energy (eigenvalues), with respect to the levels shown in Scheme 1:

$$\begin{gathered}
\psi(b_2) = \delta\, 3d_{xy} - \delta'\, \psi b_2\, (P_{y1} + P_{x2} - P_{y3} - P_{x4}) \\
\psi(e) = \gamma\, 3d_{xz} - \gamma'\, \psi_{xz}\, P_{x5} - \gamma''\, (P_{z1} - P_{z3}) \qquad (1) \\
\psi(e) = \gamma\, 3d_{yz} - \gamma'\, \psi_{yz}\, P_{y5} - \gamma''\, (P_{z2} - P_{z4}) \\
\psi(a_1) = \beta\, d_{z^2} - \beta'\, \psi a_1 \\
\psi(b_1) = \alpha\, 3d_{x^2-y^2} - \alpha'\, \psi b_1\, (\sigma_1 - \sigma_2 - \sigma_3 - \sigma_4)
\end{gathered}$$

$$\alpha^2 + \alpha'^2 - 2\alpha\alpha'\mathbf{S} = 1 \qquad (2)$$

where **S** is the appropriate overlap; for example, for Ψb_1,

$$\mathbf{S} = \langle d_{x^2-y^2} | \Psi b_1 \rangle \qquad (3)$$

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Thus the other molecular orbitals can be written as

$$\beta' = \sqrt{1-\beta^2}, \quad \gamma' = \sqrt{1-\gamma^2}, \quad \delta' = \sqrt{1-\delta^2}$$

In a first approximation, the hyperfine structure (hfs) in an ESR spectrum is considered to be a direct measurement of the coefficients in the molecular orbital, whereas the g shifts from the free spin value indirectly yield information about the orbital energy levels. The excitation energy from $\psi(b_2)$ to $\psi(b_1)$ denoted by $\Delta E_{x^2-y^2}$ is independent of the tetragonal distortion and is determined by the splitting (10 Dq) in an average octahedral environment.[6] In contrast, the energy from $\psi(b_2)$ to $\psi(e)$, ΔE_{xz}, is zero for the octahedral symmetry and becomes positive as the V=O bond shortens with respect to the bonds in the basal plane.

Next, the expression for the principal components of the **g** tensor is given. Neglecting small terms and using second-order perturbation theory, it is possible to find[13–18] the terms $g_{\|}$, $g_{\perp}$, $A_{\|}$, and $A_{\perp}$ as derived parameters for vanadyl–porphyrins. These may be written as follows:

$$\Delta g_{\|} = g_{\|} - g_e = -8\lambda\alpha^2\delta^2/\Delta E_{x^2-y^2} \tag{4}$$

$$\Delta g_{\perp} = g_{\perp} - g_e = -2\lambda\gamma^2\delta^2/\Delta E_{xz} \tag{5}$$

where $g_e =$ is the free electron g value and λ is the spin–orbit coupling constant of the free ion, $A_{\|} = E(b_1) - E(b_2)$ is the parallel electronic transition, and $A_{\perp} = E(e) - E(b_2)$ is the perpendicular electronic transition.

The ratio is

$$B = \Delta g_{\|}/\Delta g_{\perp} = 4\alpha^2\Delta E_{xz}/\gamma^2\Delta E_{x^2-y^2} \tag{6}$$

This last parameter B is a sensitive indicator of the tetragonal distortion with the shortening of the V=O bond, or with an increasing distance of the four nitrogen ligands in the basal plane. We see that ΔE_{xz} and thereby also B are increasing with respect to the limit of undistorted octahedral symmetry, and where $B = 1$ and $\Delta E_{xz} = 0$, the perturbation expression equations 4 and 5 lose their validity.

The principal components of the hyperfine tensors are given by the approximate relationships

$$A_{\|} = -K + P[-(4/7)\delta^2 - K_{\text{eff}} + (g_{\|} - g_e) + (3/7)(g_{\perp} - g_e)] \tag{7}$$

$$A_{\perp} = -K + P[(2/7)\delta^2 - K_{\text{eff}} + (11/14)(g_{\perp} - g_e)] \tag{8}$$

Furthermore, the square of the molecular orbital coefficient, δ^2, can be obtained from a suitable linear combination of the **g** and **A** tensor principal axis values by use of eqs 7 and 8,

$$\delta^2 = (7/6)\Delta g_{\|} - (5/12)\Delta g_{\perp} - (7/6)A_{\|} - A_{\perp}/P \tag{9}$$

where K_{eff} is the Fermi contact and P is proportional to the expected value of r^{-3} in the 3d orbitals of a free V^{4+} ion. Thus the product to evaluate P yields

$$P = g_e\beta_e g_n\beta_n\langle 1/r^3\rangle = 0.0117\ \text{cm}^{-1} \tag{10}$$

The quantity $C = (1 - \delta^2)$ corresponds to the fraction of unpaired electrons (i.e., delocalization over ligand orbital) and is used below to discuss the properties of the vanadyl–porphyrin structure. The ESR parameters may be also interpreted in terms of the electron delocalization from vanadium, for example by a plot of $(1 - \delta^2) \times 10^2$ vs $A_{\|}/A_{\perp}$ as is shown in Figure 3. The significance of this effect is that there is more axial bonding with more delocalization of the $3d^1$ electron from the vanadium atom.

The Fermi contact parameter, K_{eff}, can be obtained from eq 8 by inserting eq 9, and the obtained values are listed in Table 1; the names of the samples arise from the corresponding names of the oil wells from which they were collected.

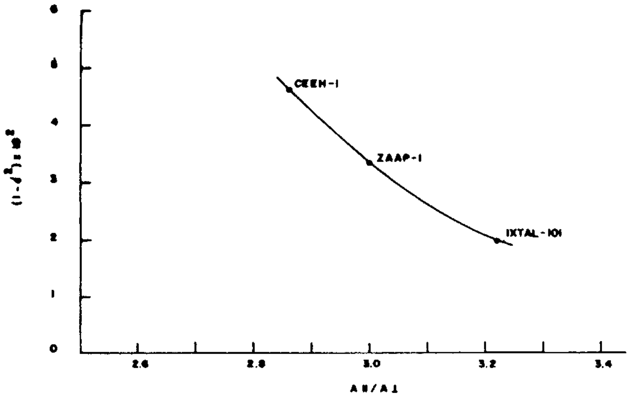

Figure 3. Values of $(1 - \delta^2) \times 10^2$ plotted vs $A_{\|}/A_{\perp}$ for VOP in frozen CH_2Cl_3 the charge delocalization increases in VOETP from Ixtal-101.

Table 2. Derived ESR Parameters for Vanadyl–Porphyrins[a] in Heavy Crude Oils

system		δ^2	K	$\Delta_{\|}/\alpha^2$	$\Delta_{\perp}/\gamma^2$
Ixtal-101	VO Porphy	0.9841	0.0086	29 498	15 408
Zaap-1	VO Porphy	0.9664	0.0080	25 862	19 108
Ceeh-1	VO Porphy	0.9538	0.0080	26 408	17 441
TBP[b]	VO Porphy	0.9600	0.0080	28 500	16 600
Etio[c]	VO Porphy	0.9841	0.0086	29 498	18 050

[a] Energies in cm^{-1}. [b] References 19 and 20. [c] References 20 and 21.

Results and Discussion

The results of the calculations are shown in Table 2. The unreduced energies are plotted as curves b_1 and e (with respect to b_2 as zero) (see Figure 4). For the calculations λ and P values were chosen as 150 and 0.0117 cm^{-1}, respectively, for the calculations and considering a positive charge of 1.5 on the vanadium atom.[13–18] This choice was made so that α^2 did not exceed unity[18] and considering the fact that the vanadium atom is out of the plane. The obtained value of 0.90 may be interpreted as a result of the overlap of the d_{xy} atomic orbital from the metal with the b_{2u} orbital combination from the porphyrin fragment, which involves the conjugated π system. Following Kilvenson and Lee's study[6] of vanadyl–porphyrin the values of K are found to be in the range 0.008–0.009 cm^{-1}, and α^2 and γ^2 have values of 0.75 and 0.60, respectively.

The unreduced energies b_1 and e were corrected to new values, denoted by b_1' and e′, by multiplying by a factor α^2. These results are predicted by the MO theory.[19–24] When α^2 and γ^2 are assumed to be 0.75 and 0.60, respectively, the corrected orbital energies b_1' and e′ have the values shown in Figure 4, regardless of the absolute positions of the orbital energies.

The analysis of the coefficients for vanadyl–porphyrin indicated that the ionic or covalent character of each bond in the qualitative ESR study of its complexes was as follows: A value of α^2 closer to 1.0 indicates a more ionic character of the bond, and a covalent character is indicated by a value of γ^2 around 0.5.

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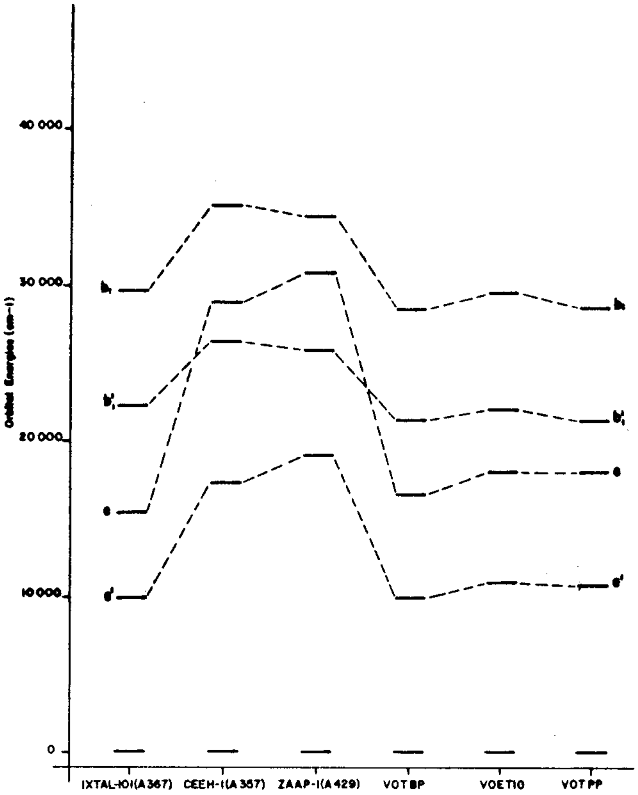


Figure 4. Calculated unreduced and corrected orbital energies for the various vanadyl porphyrins.

Table 3. Ionic or Covalent Character of V=O in Isolated Porphyrins

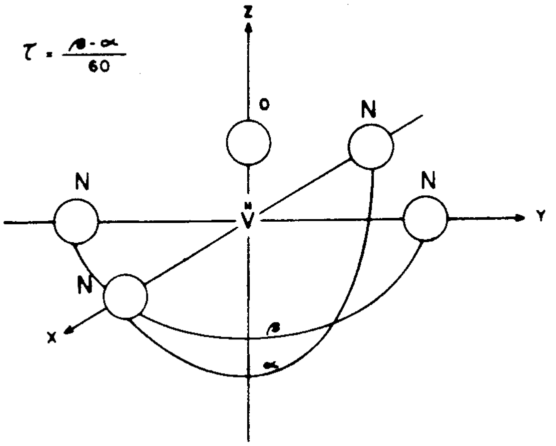
sample	π in the plane d_{xy}	σ in the plane $d_{x^2-y^2}$	π out the plane d_{xz}, d_{yz}
Ixtal-101 VO Porphy	highly ionic	moderately ionic	ionic-covalent
Zaap-1 VO Porphy	highly ionic	moderately ionic	ionic-covalent
Ceeh-1 VO Porphy	highly ionic	moderately ionic	ionic-covalent

The orbital interactions can be summarized as follows: the orbital $d_{x^2-y^2}$ (orbital in the plane) can be considered to be moderately ionic, the set of orbitals d_{xz}, d_{yz} (orbitals out of the plane) are of an ionic-covalent type, and the orbital d_{xy} (in the plane) is a highly ionic bond. (See Table 3.)

Deviations from C_{4v} symmetry are likely to occur for the individual ion, which results in nonaxially symmetry **g** and **A** tensors ($g_x \neq g_y$ and $A_x \neq A_y$). The fact that the observed spectra are well reproduced by an axially symmetric spin Hamiltonian shows that the average over the geometries corresponds to a C_{4v} symmetry.

The structural chemistry of V^{4+} molecules is well established as well as that of V^{5+}; the main feature is that the complexes of the first one adopt a square pyramidal or distorted square pyramidal geometry. We have used the angular structural parameter τ, which is defined in Scheme 2,[14] in order to compare in a qualitative fashion the purely square pyramidal structure in terms of their relative geometries about the vanadium atom, in agreement with Cornman et al.[25] For purely square pyramidal complexes τ is zero. Therefore, for our purposes, we are using complexes with $0 \leq \tau \leq 0.5$ as distorted square pyramids while complexes with $0.5 < \tau \leq 1$ have been described by Cornman et al.[25] and Smith, II, et al.,[26] as distorted trigonal bipyramids. This implies that the macrocycle with four ligands in vanadyl porphyrins in which the heteroatom donors remain constant but the geometry about the metal varies provides a weaker ligand field and suggests that there are electronic and or steric requirements that preclude the formation of trigonal bipyramid geometry to V^{4+}.

Scheme 2. Structure of Ion VO^{2+} in Porphyrins



The characteristics of the V=O bond in the porphyrin from the Zaap-1 and Ceeh-1 oils correspond to a strengthening, which means a low average of tetragonal distortion, and we assume that this can be attributed to steric or electronic requirements. A_{xx}, A_{yy}, and A_{zz} do not correlate with τ; however, the difference $|A_{xx} - A_{yy}|$ generally increases with τ. Vanadyl−porphyrins in Ixtal-101, Zaap-1, and Ceeh-1 are axial and the differences $|A_{xx} - A_{yy}|$ are 5.2×10^{-4}, 4.0×10^{-4}, and 4.16×10^{-4} cm^{-1}, respectively.

The A_{xx} is the most sensitive parameter for variations in structure. A_{xx} varies as 51.0×10^{-4}, 48.0×10^{-4}, and 45.0×10^{-4} cm^{-1} (A_{xx} average 49.3×10^{-4} cm^{-1} $\pm$ 2.3×10^{-4} cm^{-1}) (error expressed as standard deviation). On the other hand, A_{yy} varies as 55.9×10^{-4}, 52.0×10^{-4}, and 49.1×10^{-4} cm^{-1} (A_{yy} average 52.3×10^{-4} cm^{-1} $\pm$ 0.35 cm^{-1}). The sensitivity of A_{xx} is intuitively appealing since the structure changes most along the molecular x axis.

The relations between the spin Hamiltonian parameters (**g** and **A**) and the electronic structure of d^1 complexes in various symmetries have been described nicely by Mabbs and Collison.[27] These relations are shown in eqs 11 and 12, where δ is the one-electron spin−orbit coupling constant for vanadium(IV) and δ_{ij} is the Kronecker delta.

$$g_{ij} = 2.0023\delta_{ij} - 2\lambda\Lambda_{ij} \tag{11}$$

$$A_{ij} = P - k\delta_{ij} - 3cl_{ij} - 2\lambda\Lambda_{ij} + 3c\delta\Lambda'_{ij} \tag{12}$$

The terms Λ_{ij} and Λ_{ij}' in the theoretical model lead the spin−orbit coupling to mix the excited with the ground states and reintroduce the orbital contribution to the g value. If spin−orbit interactions are introduced as a perturbation, then, to the first approximation, the g shift is directly proportional to both coefficients of the ground and the excited state MO and inversely proportional to the energy differences. The term $3cl_{ij}$ is dependent only on the ground state and is the same for A_{xx} and A_{yy}. Considering only the vanadyl porphyrin complexes which are anticipated to have C_{4v} symmetry in solution and frozen

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solution, it is seen in Table 1 that g_{xx} and g_{yy} are not sensitive (within error) to change in structure. Thus, the changes in structure have very little influence on the Λ_{ij} in eq 11. Accordingly, A_{xx} and A_{yy} are only slightly influenced by changes in structure as it is manifested in $-2\lambda\Lambda_{ij}$ (eq 10). Since g_{ij} are $-2.0023 = -2\lambda\Lambda_{ij}$ ($g_{ij} - 2.0023 = -0.039$ to -0.022 for $ij = xx$ or yy), in vanadyl porphyrins of Ixtal-101, Zaap-1 -0.033 to -0.014 and Ceeh-1 -0.031 to -0.015, the contribution of this term to A_{xx} and A_{yy} is $= 3.5 \times 10^{-4}$ to 2.7×10^{-4} cm^{-1}, 2.6×10^{-4} to 1.64×10^{-4} cm^{-1}, and 2.76×10^{-4} to 1.8×10^{-4} cm^{-1}, respectively (assuming $P = 150 \times 10^{-4}$ cm^{-1}). Therefore, the decrease in A_{xx} observed must be predominantly due to the effects of $\Lambda'_{ij.}$ The difference $A_{xx} - A_{yy}$ is related to $\Lambda_{ij} - \Lambda'_{ij}$ as is shown in eq 13.

$$\begin{aligned} A_{xx} - A_{yy} &= P[-2\lambda\,\Lambda_{xx} - (-2\lambda\Lambda_{yy}) + 3c\lambda(\Lambda'_{xx} - \Lambda_{ij}{}')] \\ &= P[g_{xx} - g_{yy} + 3c\lambda(\Lambda'_{xx} - \Lambda'_{yy})] \qquad (13) \end{aligned}$$

This difference must also be due, in large part, to the Λ'_{ij} terms since $P(g_{xx} - g_{yy})$ is small for vanadyl porphyrins in Ixtal-101, Zaap-1, and Ceeh-1 (0.8×10^{-4}, 0.96×10^{-4}, and 1.0×10^{-4} cm^{-1}, respectively). However, it has been known for some time that the parallel component of the hyperfine coupling constant, A_{zz}, is sensitive to the donor type in the "equatorial" coordination sphere. From this knowledge, the empirical additivity relationship[25] in eq 14 can be used as a means of determining, to a first approximation, the identity of the "equatorial" ligands in vanadyl complexes.

$$A_{zz(\mathrm{calc})} = \sum n_i A_{zi} \qquad (14)$$

Here n_i is the number of equatorial ligands of type i and A_{zj} is the empirically determined contribution from each equatorial ligand of type i. The estimated error for eq 13 is $\pm 3 \times 10^{-4}$ cm^{-1}. A_{zz} is most sensitive to the equatorial ligand influence. Comparison of the calculated and experimental values of A_{zz} can be used to argue in favor of or against the presence of specific ligands.[29−32]

The empirical parameters A_{zi} in eq 14 have been determined for molecules of assumed square pyramidal geometry. However, the applicability of eq 14 from structurally distorted molecules has been reevaluated recently,[30] thereby supporting the continued use of eq 14 for vanadyl complexes and the values for A_{zj} in refs 6 and 24; these are $A_{zz(\mathrm{calc})} = 158 \times 10^{-4}$ cm^{-1} for vanadyl porphyrins and meso porphyrin methyl ester, 157×10^{-4} cm^{-1} for vanadyl etioporphyrin in crude oil and tar sand, and 150×10^{-4} cm^{-1} for synthetic vanadyl tetrabenzoporphyrin. The difference $A_{xx} - A_{yy}$ is related to $\Lambda_{ij} - \Lambda_{ij}{}'$ as is shown in eq 13.

The values are very close to the experimental values for A_{zz} (Table 1) as the structure varies in the natural vanadyl porphyrins Ixtal-101, Zaap-1, and Ceeh-1. The values for A_{zz} are 157×10^{-4}, 145×10^{-4}, and 144×10^{-4} cm^{-1}, respectively ($A_{zz(\mathrm{av})} = (150 \pm 1.7) \times 10^{-4}$ cm^{-1}). The small variation in A_z (1.9% of A_{zz}) suggests that eq 14 also holds for the distorted molecules such as vanadyl porphyrin complexes to make a first estimate of the equatorial ligands.

Differences in Contribution to $A_{\|}$ Depending on Orientation. By taking the (VO (Salim H)− (Sal)) complex and subtracting from its $A_{\|}$ the known value for phenolate an $A_{\|}$ 123.7×10^{-4} cm^{-1} is obtained for a (Salim H) ligand as a whole. This value is then subtracted from the $A_{\|}$ of vanadyl porphyrin from our samples, i.e., 157×10^{-4} cm^{-1} for Ixtal-101, 145×10^{-4} cm^{-1} for Zaap-1, and 144×10^{-4} cm^{-1} for Ceeh-1 in order to obtain values for the pyrrole bonds. The $A_{\|}$ values for these complexes fell into the two groups: one clustered around 33.3×10^{-4} cm^{-1} for Ixtal-101 and two around 21.3×10^{-4} and 20.4×10^{-4} cm^{-1} for Zaap-1 and Ceeh-1, respectively (Table 3). We also observed that the lower values for $A_{\|}$ indicate that pyrrole rings are bound in a parallel position to the vanadyl group and the higher values $A_{\|}$ are found where pyrrole rings are bound in a perpendicular position to the vanadyl group or parallel to the equatorial plane of the porphyrin.

Equatorial vs Axial Ligand Preference of Pyrrole to VO^{2+}. One of the original goals of the research by Pecoraro and co-workers[26] was to synthesize a vanadyl complex with an imidazole in axial position, as there is in the VCLPO crystal structure. Because vanadyl complexes prefer oxyanions with respect to neutral amines, one might expect that the worst donor ligand (imidazole) would fill the axial position. The other functional group would bind equatorially because it is a better donor than imidazole. The group also should coordinate at a sufficiently low PH to minimize the possibility of oxidation of vanadium(IV) to vanadium(V).

This behavior shown in the last paragraph can be explained and applied at the same time as well in imidazole as pyrrole ring by considering the p (aromatic) orbital on the donating nitrogen atom (see Figure 2). The imidazole or pyrrole ring will only assume a conformation perpendicular to the vanadyl unit in the equatorial plane when it is constrained by being part of a planar ligand. In the perpendicular conformation, the donating nitrogen p orbital (and, hence, the imidazole or pyrrole aromatic molecular orbital) can only interact with the coordination sphere of the best π donor, i.e., the vanadyl oxygen atom (bound to the d_{xz}, d_{yz} atomic orbitals from the metal atom). The imidazole or pyrrole ring will prefer not to coordinate in the axial position for the same reason. The orbital overlap between the p orbitals from the nitrogen atoms and the vanadium d_{xy} is optimized only when the imidazole or pyrrole ring coordinates equatorially and parallel to the vanadyl group, and its unfavorable interaction with d_{xz} and d_{yz} orbitals is minimized. We conclude that vanadyl complexes composed of sterical nondemanding ligands which contain coordinated imidazole or pyrrole will obey this trend for the orientation of imidazole or pyrrole. An imidazole or pyrrole oriented parallel to the vanadyl unit for best orbital overlap would be a better π donor, and so would have a lower contribution to $A_{\|}$. This topic combined with the observed $A_{\|}$ values supports the conclusion by Pecoraro and co-workers[26] that reports the value of 40×10^{-4} cm^{-1} for $[\mathrm{VO(im)_4}]^{2+}$; this feature means that all four imidazole units are bound parallel to the vandyl. This preference for equatorial binding with parallel orientation also holds true for $[\mathrm{VO(pyr)_4}]^{2+}$ in Ixtal-101, Zaap-1, and Ceeh-1 crude oils, respectively, with a similar trend for pyrrole units parallel to the vanadium oxygen double bond, and it was found to have a contribution of $A_{\|}$ of 33.3×10^{-4}, 21.3×10^{-4}, and 20.4×10^{-4} cm^{-1}.

Unusually high $A_{\|}$ are reported by Crans[28] and co-workers for (*N*-benzimidazol-2-ylmethyl)imino(ethanol)-(ethanolato)-

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Table 4. Tetragonal Distortion Degree to V═O in Isolated Porphyrins

sample	$\Delta g_{\parallel}/\Delta g_{\perp}$	L(V−O)[a]	L(V−N)[a]
VO in Porphyrin Ixtal-101	3.22	> strengthening	≫lengthening
VO in Porphyrin Zaap-1	3.00	< strengthening	< lengthening
VO in Porphyrin Ceeh-1	2.86	≪strengthening	< lengthening
VO in ETIO Porphyirin[c]	2.33	< strengthening	< lengthening
VO in TBP porphyrin[b]	2.44	< strengthening	< lengthening

[a] L(V−O) and L(V−N) = ligand vanadium−oxygen and vanadium nitrogen. [b] References 19 and 20. [c] References 20 and 21.

(acetylacetonato)oxovanadium(IV), and they suggest that a possible cause is the distortion in this kind of complex. Because this complex contains a coordinated alkoxide group, and because EPR is carried out in a DMF/water solution, it could be possible that the alkoxide has been protonated and/or exchanged for a solvent molecule, which would provide one explanation for unusually high $A_{\parallel}$.

In another pathway the ESR parameters allowed us to make an estimation of the geometrical changes in different vanadyl−porphyrin structures, The ratio $B = \Delta g_{\parallel}/\Delta g_{\perp}$ reflects small changes of the tetragonal distortion as it was indicated in the previous section; therefore, an increase of B indicates a shortening of the V═O bond or a lengthening of the distances to the nitrogen ligands in the basal plane.

Thus, the geometry changes are consistent with an increase in B. The distortion values shown for B in Table 4 correspond to a synthetic vanadyl−porphyrin,[19−24] and the results of the natural isolated vanadyl−porphyrin can be interpreted as a criterion for this distortion. For example, the crude oil named as Zaap-1 shows a V═O large bond strength whereas the charge variation due to the electron delocalization ($I - \delta^2$) onto the orbital ligand is not significant. A different effect is seen for the Ceeh-1 crude oil, where we found a weaker V═O bond, and also no important changes for the corresponding charge due to the electron delocalization are appreciated.

However, the tetragonal distortion observed for V═O in the porphyrin from the Ixtal-101 crude oil sample is the largest, and this indicates a lower V═O bond strength; similarly, this sample exhibits the largest electronic delocalization (this effect means we have the short bonds in all the analyzed samples). Then, according to Figure 3, the large charge delocalization of the vanadyl aetioporphyrin (VOETP) in solution[33−36] can be explained by charge transfer from the π system on the alkylated porphyrin ring. The resulting decrease of electron density in the porphyrin ring promotes electron delocalization on the vanadium atom.[33]

The values for $g_{\parallel}$ and $g_{\perp}$ shown in Table 1 for the samples of isolated vanadyl−porphyrin can help to establish the predominance of the compounds. The degree of distortion increases its value as B increases, and this phenomenon can be attributed to the role of the different orientation of pyrrole rings bound parallel or perpendicular to the vanadyl group and the alkylated chains around the porphyrin macrocycle molecules which are predominant in the pure mixture. This trend is as follows: Ixtal-101 > Zaap-1 > Ceeh-1. This is consistent with the average tetragonal degree of distortion for each sample, $B = 3.22$, $B = 3.00$, and $B = 2.86$ (see Table 4). Therefore we show results that correspond to a strengthening or a lengthening of the V═O bond. The short V═O bond in vanadyl−etioporphyrin from Ixtal-101 crude oil is caused by an increase in the electron density in the axial bond and more electron delocalization to the $3d^1$V orbital.

With respect to the origin of the Fermi contact term for the 3d orbital in the ion V^{4+}, an electron in the $\psi^*(b_2)$ orbital, defined by eq 1, does not give rise to a Fermi contact interaction directly, as the wave function vanishes at the nucleus. However, the unpaired electron density precludes the polarization of the core s electrons,[14] which results in an indirect hyperfine interaction. Note that the term $-PK_{\text{eff}}$ in eq 8 represents the main negative contributions for both $A_{\parallel}$ and $A_{\perp}$.

Some authors[37] have discussed the influence of electron delocalization on the Fermi contact term. Following their notation K_{eff} can be split into two contributions.

$$K_{\text{eff}} = \delta^2 K_1 + (1 - \delta^2) K_2 \qquad (15)$$

Here $\delta^2 K_1$ represents the core of polarization due to the electron density in the $3d_{xy}$ orbital; this is the only contribution considered by Kivelson and Lee.[6] The second term in eq 15, $(1 - \delta^2)K_2$, arises due to the electronic density delocalized into other orbitals of the vanadium atom. Our data does not provide information on the mechanisms that contribute to K_2; however, experimentally we observe (Table 1) that K_{eff} is practically independent of δ^2, and this implies that K_1 and K_2 must be of equal magnitude.

Conclusions

This study was derived from experimental ESR studies and helps to give a better understanding of the electron structure of the vanadium atom in natural porphyrin series obtained from heavy crude oils.

The analysis of the spectra was based on the fact that we found a tetragonal (C_{4v}) distorted average coordination geometry. The increase of the tetragonal distortion, which is due either to shortening of the V═O bond or to an increase of the ligand distance in the basal plane, corresponds in both cases to a higher bond strength. Using the parameters α, δ, and γ allowed us to obtain an estimation of the covalent or ionic character of the V−N ligand bonds. Estimations of the V═O bond strength and the delocalization of the unpaired electrons V^{4+} onto the coordinative bond nitrogen belonging to the ligand have been also obtained from the spectra.

The trend observed in vanadyl porphyrins with all equatorial ligands equivalent is derived if the molecule is described as having four pyrrole groups bound in equatorial position, but with different orientations with respect to the vanadyl group, and shows a tendency based on observed $A_{\parallel}$ of the angle between the pyrrole ring and the vanadyl group. Pyrrole rings bound in a parallel position to the vanadyl group have a contribution to $A_{\parallel}$ of approximately 21.3×10^{-4} and 20.4×10^{-4} cm^{-1} whereas the contribution for perpendicular pyrrole rings is close to 33.3×10^{-4} cm^{-1}. This trend could be explained by considering the overlap of the pyrrole nitrogen p orbital with the vanadium nonbonding d_{xy} orbital (favorable) and with the vanadium d_{xz} and d_{yz} orbitals (unfavorable) supported by examination of metal bonding character. This explanation leads to the next conclusion. Vanadyl porphyrins can readily adopt small tetragonal distortion from the more common square pyramidal geometry. EPR spectroscopy is sensitive to these structural perturbations, and this feature can be probed through the associated increase of

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the difference $|A_{xx} - A_{yy}|$ with the increasing in the square pyramidal geometry nature of the complexes. The parallel coupling constant A_{zz} is relatively insensitive to these structural changes, and this indicates that EPR additivity relationships can be applicable to distorted vanadyl−porphyrins.

It is interesting to note that the Fermi contact term, K_{eff}, is essentially constant for all samples investigated and is found to be independent of electron delocalization $(1 - \delta^2)$; it varies only slightly among the three oil samples. The orbital energy values derived from the ESR studies are in agreement with those predicted from MO theory for synthetic vanadyl−porphyrins.

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