# Structural Information from ENDOR Spectroscopy: The Frozen Solution Proton Spectra of Some VO(II) Complexes

## **Donato Attanasio**

Istituto di Teoria e Struttura Elettronica dei Composti di Coordinazione del C.N.R., 00016 Monterotondo Staz., Rome, Italy (Received: December 27, 1985; In Final Form: April 16, 1986)

The frozen solution proton ENDOR spectra of an extensive series of vanadyl Schiff base complexes have been measured at ca. 100 K. The experimental couplings have been assigned to specific protons by means of chemical substitution. The principal values of the hyperfine tensors have been obtained after transformation of the measured hyperfine components in the limit of the point dipole approximation (axially symmetric tensors). In this way both the distance and the orientation of the interacting protons could be estimated. Comparison with existing literature indicates that rigid matrix ENDOR gives structural information with comparable accuracy but, sometimes, higher resolution than single-crystal ENDOR.

#### Introduction

Ligand hyperfine splittings are usually unresolved in the EPR spectra of d<sup>1</sup> VO(II) and MoO(III) complexes,<sup>1-5</sup> whereas a variety of data, from many different ligand atoms, have been obtained from the well-resolved spectra of several oxo-transfer Mo enzymes.<sup>6,7</sup>

These results, in spite of their invaluable contribution to the interpretation of enzymatic mechanisms, have given limited structural information. This is partly due to the absence of comparative data on simple compounds of known geometry. Therefore, we are currently testing the possibility of obtaining this kind of information with the aid of ENDOR spectroscopy of nonoriented samples.

Recently several groups have shown renewed interest in this technique.<sup>8-13</sup> As a matter of fact proper interpretation of powder ENDOR data, both hyperfine and quadrupole, has been shown to characterize quite general cases of magnetic couplings.<sup>10,11</sup> Therefore in the case of complex paramagnetic systems, usually not available in single-crystal form, ENDOR spectroscopy may considerably extend the kind of information obtainable through simple EPR spectroscopy, and is one of the few techniques available to give an insight into the electronic and geometrical structure of the metal ion binding site. Apart from metalloenzymes pertinent examples include metal supported or intercalated materials of catalytic interest, where the understanding of structure activity correlations is a goal of primary relevance.<sup>12,13</sup>

This report focuses on the interpretation and the extraction of structural parameters from the frozen solution spectra of simple coordination compounds of VO(II), an ion which has widely been used as an EPR probe in the study of the metal ion binding sites of a variety of biological systems.<sup>14</sup> Work on related molybdenum species, in which case additional problems are the low anisotropy of the g tensor and the low symmetry of the compounds, is in progress and will be reported elsewhere.<sup>15</sup>

- (1) Goodman, B. A.; Raynor, J. B. Adv. Inorg. Chem. Radiochem. 1970, 13, 135.
- (2) Kokin, R. P. Magn. Reson. Rev. 1979, 5, 75
- (3) Chasteen, N. D. Coord. Chem. Rev. 1977, 22, 1.
- (4) Stiefel, E. I. Prog. Inorg. Chem. 1977, 22, 1.
   (5) Scullane, M. J.; Taylor, R. D.; Minelli, M.; Spence, J. T.; Yamanouchi, K.; Enemark, J. H.; Chasteen, N. D. Inorg. Chem. 1979, 18, 3213.
- (6) Bray, R. C. In Biological Resonance; Berliner, L. J., Reuben, J., Eds.; Plenum: New York, 1979; Vol. 2, p 45.
  - (7) Spence, J. T. Coord. Chem. Rev. 1983, 48, 59.
  - (8) van Willigen, H.; Kirste, J. Phys. Chem. 1982, 86, 2743.
- (9) Hoffman, B. M.; Venters, R. A.; Roberts, J. I. J. Am. Chem. Soc. 1982. 104. 4711.
- (10) Hoffman, B. M.; Martinsen, J.; Venters, R. A. J. Magn. Reson. 1984,
- (11) Hoffman, B. M.; Venters, R. A.; Martinsen, J. J. Magn. Reson. 1985, 62, 537.
- (12) van Willigen, H.; Chandrashekar, T. K. J. Am. Chem. Soc. 1983, 105, 4232.
- (13) van Willigen, H. J. Phys. Chem. 1983, 87, 3366. (14) Chasteen, N. D. In Biological Magnetic Resonance; Berliner, L. J., Reuben, J., Eds.; Plenum: New York, 1981; Vol. 3 p 53.
- (15) Attanasio, D., unpublished results.

#### **Experimental Section**

The oxovanadium(IV) derivatives of the tetradentate Schiff base ligands N,N'-ethylenebis(acetylacetone imine), N,N'ethylenebis(salicylideneamine), and N, N'-o-phenylenebis(salicylideneamine), i.e., VO(acen), VO(salen), and VO(salphen), see Figure 1, were prepared and purified by standard literature procedures.<sup>16-19</sup> Similar methods were used to obtain the complexes of the substituted ligands 3-CH<sub>3</sub>Osalen, 5-Clsalen, 7-CH<sub>3</sub>salen, and 3-CH<sub>3</sub>Osalphen.

Analytically pure samples were obtained after recrystallization from toluene or CH<sub>3</sub>OH [VO(salen) and VO(3-CH<sub>3</sub>Osalen)) or  $CH_3CN$  (VO(5-Clsalen and VO(salphen)]. Three out of seven compounds turned out to be solvated species and are formulated on the basis of analytical, thermogravimetric, and IR data as  $VO(3-CH_3Osalen)(H_2O)_2$ ,  $VO(3-CH_3Osalphen)(H_2O)$ , and VO(salphen)(CH<sub>3</sub>CN). The former compound easily loses lattice water at room temperature under vacuum, whereas the latter require higher temperatures (140 and 130 °C respectively).

EPR and ENDOR spectra were obtained at ca. 100 K from frozen solution samples. The concentrations ranged from 1 to  $2 \times 10^{-2}$  M and the solvent was generally a mixture of dimethylformamide- $d_7$  and chloroform-d, which assures both high solubility and satisfactory glass formation. Occasionally toluene- $d_8$ or pyridine- $d_5$  were used in place of DMF- $d_7$ . Sample preparation was usually carried out in the air, but in the case of the solvated complexes solutions of the anhydrous parent compounds were prepared and manipulated in a M. Brown, Model MB-200, drybox.

The spectra were recorded on a standard Varian E-9 Spectrometer equipped with variable-temperature and ENDOR, Varian E-1700 BB, accessories. Magnetic fields and microwave frequencies were measured, respectively, with a Bruker BNM 20 gaussmeter and with a Systron-Donner 6246A counter. ENDOR spectra were recorded in the FM modulation scheme, and no field modulation was employed. Typical settings were microwave power 10 mW, rf power 100 W, frequency modulation 10 kHz, frequency modulation depth 20-50 kHz. Spectra recorded below 100 K, with the aid of an Oxford Instrument ESR 9 cryostat, showed a much larger S/N ratio, but only a limited resolution improvement.

#### Results

Typical rigid matrix EPR spectra of the Schiff base VO(II) complexes are presented in Figure 2. Some of these spectra have been already reported, and our spin Hamiltonian parameters, Table I, do not differ significantly from those in the literature.<sup>16,19</sup> The magnetic symmetry is almost perfectly axial in the case of

- (18) Pfeiffer, P.; Hesse, T.; Pfitzner, H.; Scholl, W.; Thiebert, H. J. Prakt. Chem. 1937, 149, 217.
- (19) Boucher, L. J.; Tynan, E. C.; Yen, T. F. In ESR Spectra of Metal Complexes; Yen, T. F.; Plenum: New York, 1969; p 111.

<sup>(16)</sup> Boucher, L. J.; Tynan, E. C.; Yen, T. F. Inorg. Chem. 1968, 7, 731.

<sup>(17)</sup> Selbin, J.; Manning, H. R.; Cessac, G. J. Inorg. Nucl. Chem. 1963, 25. 1253.

TABLE I: X-Band Spin Hamiltonian Parameters of VO<sup>2+</sup> Schiff Base Complexes in Chloroform/Dimethylformamide (1:1) at ca. 300 and 100 K<sup>a</sup>

 compound	g <sub>iso</sub>	<b>g</b> <sub>ll</sub>	g	Γ.	A <sub>iso</sub> V	$A_{\parallel}^{v}$	A	⊥ <sup>V</sup>	
VO(acen)	1.979	1.956	1.987		91.7	162.5	57.0		
VO(salen)	1.977	1.958	1.982	1.991	90.1	158.3	54.9	51.7	
VO(3-CH <sub>3</sub> Osalen)	1.978	1.958	1.982	1.990	90.0	159.0	55.9	52.8	
VO(5-Clsalen)	1.976	1.957	1.982	1.990	90.0	158.3	55.9	52.4	
VO(7-CH <sub>3</sub> salen)	1.977	1.952	1.985	1.991	89.6	155.5	55.3	53.0	
VO(salphen)	1.978	1.958	1.983	1.988	90.0	159.4	55.9	53.6	
VO(3-CH <sub>3</sub> Osalphen)	1.979	1.958	1.982	1.988	90.4	161.0	56.2	53.9	

<sup>a</sup> Hyperfine parameters in units of  $10^{-4}$  cm<sup>-1</sup>. Experimental errors, g values  $\pm 0.001$ ;  $A^{V}$  values  $\pm 0.5 \times 10^{-4}$  cm<sup>-1</sup>.



 $X_3 = H$ salphen  $X_3 = CH_3O$ 3-CH<sub>3</sub>O salphen

Figure 1. Molecular structures of the Schiff base vanadyl complexes.

VO(acen), but shows the presence of small rhombic distortions in all the other compounds.

As already pointed out in the literature<sup>20-22</sup> the strong anisotropy of the vanadyl hyperfine splitting (hfs) tensor, together with its quasi-axial symmetry, offers the opportunity to obtain well-resolved single-crystal-like ENDOR spectra, with high orientational selectivity, by saturating properly selected turning points in the EPR spectrum. Field settings z and xy in Figure 2 indicate the EPR peaks which were saturated to obtain, respectively, parallel and



Figure 2. Typical frozen solution X-band EPR spectra (100 K) of the Schiff base vanadyl complexes. z and xy indicate the turning points which have been saturated to obtain parallel and perpendicular ENDOR spectra.

**TABLE II: Experimental Proton Hyperfine Splitting Components** (MHz) of VO(acen)<sup>a</sup>

proton	$A_{z}^{H}$	$A_x^{H}$	$A_y^{H b}$	
CH3	0.69	0.71	1.51	
CH <sub>3</sub> ′	0.50	0.50	1.30	
CH	0.93	n m <sup>c</sup>	n m <sup>c</sup>	
CH <sub>2eq</sub>	2.38	2.11	3.76	
CH <sub>2ax</sub>	2.90	2.84	5.06	

<sup>a</sup>Spectra recorded in CDCl<sub>3</sub>:DMF- $d_7$  (1:1), 100 K. <sup>b</sup>x, y, and z refer to the g principal axis system. cn m = not measured.

perpendicular ENDOR spectra (where  $\parallel$  and  $\perp$  refer to the V=O bond direction). This choice is not unique and saturation of different hyperfine lines gave quite similar results. However, no attempt was made to study the ENDOR spectra as a function of the systematic change of  $B_0$ .

Figure 3 shows the parallel ENDOR spectra of the acen, salen, and substituted salen complexes. Their molecular structures are sketched in Figure 1. In these single-crystal-like spectra each set of equivalent protons gives rise to a pair of lines at  $v = |v_p \pm 1/2A_z|$ where  $v_p$  is the free proton frequency and  $A_z$  is the effective hyperfine component measured along the z direction of the g (or metal hyperfine) axis system. The experimental peaks and the corresponding  $A_z$  values (Tables II and III) have been assigned to specific protons on the basis of literature data, chemical substitution at selected positions, and comparison of known and spectroscopically obtained metal proton distances (see below).

The spectrum of VO(acen), compared with the results reported by van Willigen et al. in the case of VO(acac),<sup>8,23,24</sup> shows the presence of two extra pair of lines which must be attributed to the axial and equatorial protons of the ethylenediamine bridge.

<sup>(20)</sup> van Willigen, H. J. Magn. Reson. 1980, 39, 37.

 <sup>(21)</sup> Schweiger, A. Struct. Bonding 1982, 51, 1.
 (22) Atherton, N. M.; Shackleton, J. F. Mol. Phys. 1980, 39, 1471.

<sup>(23)</sup> van Willigen, H. Chem. Phys. Lett. 1979, 65, 490.

<sup>(24)</sup> van Willigen, H.; Kirste, B. Chem. Phys. Lett. 1982, 87, 589.



Figure 3. Frozen solution parallel proton ENDOR spectra (100 K) of the acen- and salen-type VO(II) complexes. Different proton lines are labeled as follows: a and e, axial and equatorial ethylenediamine protons; m and m' methyl protons; 7, 3, 6, and 5 are the  $H_7$ ,  $H_3$ ,  $H_6$ , and  $H_5$  protons. The lines labeled x have not been identified.

 
 TABLE III: Experimental Proton Hyperfine Splitting Components (MHz) of VO(II) Complexes with Salen and Substituted Salen Ligands<sup>a</sup>

proton	$A_z^{H}$	$A_x^{H}$	$A_{y}^{H}$	
H <sub>3</sub>				
salen	1.03	1.01	2.02	
5-Cl	1.01	0.99	1.95	
7-CH3	1.07	1.05	2.03	
H <sub>7</sub>				
salen	1.66	1.55	3.14	
5-Cl	1.60	1.50	3.17	
3-CH <sub>3</sub> O	1.61	1.51	3.05	
H <sub>6</sub>				
salen	0.47	0.47	1.01	
5-C1	0.46	0.45	0.99	
3-CH <sub>3</sub> O	0.49	0.48	1.05	
7-CH3	0.45	0.43	1.05	
H <sub>5</sub>				
salen	0.26	n m <sup>b</sup>	n m	
3-CH <sub>3</sub> O	0.25	0.23	n m	
CH <sub>2eq</sub>				
salen	2.26	~2.3	3.91	
5-C1	2.23	2.14	n m	
3-CH <sub>3</sub> O	2.25	2.11	3.96	
7-CH3	1.86	1.35	3.70	
CH <sub>2ax</sub>				
salen	2.68	2.59	n m	
5-Cl	2.67	2.56	4.40	
3-CH <sub>3</sub> O	2.65	2.51	4.66	
7-CH3	2.78	2.54	n m	

<sup>a</sup>Spectra measured at 100 K in  $CDCl_3$ -DMF- $d_7$  or  $CDCl_3$ -py- $d_5$  mixtures. <sup>b</sup> n m = not measured.



Figure 4. Frozen solution perpendicular proton ENDOR spectra (100 K) of the acen and salen type complexes. Different proton lines are labeled as in Figure 3.

In addition, the lower symmetry of VO(acen) splits the lines due to the CH<sub>3</sub> protons, which are no longer equivalent, in two pairs. Finally, as in the spectrum of VO(acac) the CH lines are buried under the strong CH<sub>3</sub> proton peaks and are barely visible.

Inspection of the parallel spectra of VO(salen), VO(3-CH<sub>3</sub>Osalen), and VO(5-Clsalen) indicates that the position and shape of the lines due to the ethylenediamine protons undergo only minor changes within the series and with respect to VO(acen). In addition lines due to the H<sub>3</sub> and H<sub>5</sub> protons are unequivocally identified. We would expect lines due to the H<sub>4</sub> and H<sub>5</sub> protons to be very close in frequency and probably unresolved. However, the spectrum of VO(5-Clsalen) shows the lines split by 0.26 MHz to disappear completely upon H<sub>5</sub> substitution. The possibility of detecting the H<sub>5</sub> contribution in these spectra is noteworthy since the metal proton distance, in this case, is larger than 650 pm.<sup>25</sup>

The remaining two pairs of lines are reasonably attributed to the H<sub>6</sub> and H<sub>7</sub> protons. This latter assignment is confirmed by the absence of the corresponding peaks in the spectrum of VO-(7-CH<sub>3</sub>salen). Apart from this, the couplings of the ethylenediamine protons in VO(7-CH<sub>3</sub> salen) are somewhat different from those reported above ( $A_z^{ax} = 2.78$  MHz;  $Az^{eq} = 1.86$  MHz). This suggests that the presence of the CH<sub>3</sub> groups in position 7 markedly affects the conformation of the complex. The H<sub>3</sub> lines are split by 1.07 MHz, which is close to the values reported above, whereas the other ring protons give a single unresoled pair of peaks with coupling ca. 0.44 MHz.

VO(salphen) and VO(3-CH<sub>3</sub>Osalphen) show parallel ENDOR spectra, Figure 5, which are much broader and less resolved. Apart from an intense unresolved pair of peaks split by ca. 0.5 MHz and due to ring protons, VO(salphen) shows two lines split by 0.98

<sup>(25)</sup> Haller, K. J.; Johnson, P. M.; Feltham, R. D.; Enemark, J. H.; Ferraro, J. R.; Basile, L. J. Inorg. Chim. Acta 1979, 33, 119.



Figure 5. Frozen solution parallel and perpendicular proton ENDOR spectra (100 K) of VO(salphen) and VO(3-CH<sub>3</sub>oOsalphen). These samples have been prepared in nonanhydrous conditions. Different proton lines are labeled as follows: w, water protons; 3, 6, 7, and 9 are the  $H_3$ ,  $H_6$ ,  $H_7$ , and  $H_9$  protons. The line labeled x has not been identified.

MHz, which are absent in the spectrum of the 3-CH<sub>3</sub>O-substituted compound and are therefore assigned to the H<sub>3</sub> protons. Other lines are present in these spectra with splittings of 5.78 MHz in the case of VO(salphen) and 6.0 and 2.39 MHz in the case of VO(3-CH<sub>3</sub>Osalphen). These lines are due to water protons as shown by the fact that they completely disappear if the samples are prepared under anhydrous conditions (see the Experimental Section) and are immediately restored upon addition of water. The largest splitting is typical of axially coordinated water trans to the vanadyl bond, whereas the assignment of the lines split by 2.39 MHz in the spectrum of VO(3-CH<sub>3</sub>Osalphen) is more uncertain. However, literature data would support the presence of water protons hydrogen bonded to the vanadyl oxygen.<sup>8</sup>

It is worth noting that interaction with water protons has been detected for VO(3-CH<sub>3</sub>Osalphen)(H<sub>2</sub>O) and VO(salphen)-(CH<sub>3</sub>CN), but not for VO(3-CH<sub>3</sub>Osalen)(H<sub>2</sub>O)<sub>2</sub>. This shows that there is a clear-cut difference in axial ligation ability of vanadyl salen- or salphen-type complexes. In addition, the magnetic interaction observed for the salphen compound must be attributed to adventitious water present in the solvent.

Turning to the two-dimensional perpendicular ENDOR spectra, which are presented in Figures 4 and 5, the situation becomes more complicated, since two pairs of peaks are now expected for each set of equivalent protons. The splitting of these lines gives the

TABLE IV:	<b>Experimental Proton Hyperfine Splitting Components</b>
(MHz) for V	O(salphen) and VO(3-CH <sub>3</sub> Osalphen) <sup>a</sup>

proton	A <sub>z</sub> <sup>H</sup>	$A_x^{H}$	$A_y^{H}$	
H,				
salphen	0.98	1,00	1.93	
H7 .				
salphen	n m <sup>b</sup>	1.52	3.71	
3-ĊH <sub>2</sub> O	n m	1.51	3.65	
H <sub>6</sub>				
salphen	0.47	0.47	1.00	
3-ĊH₁O	0.47	0.47	1.06	
H				
salphen	n m	n m	1.52	
3-ĊH₃O	n m	n m	1.51	
H <sub>2</sub> O				
salphen	5.78	2.67	2.67	
3-ĊH₃O <sup>c</sup>	6.0	2.77	2.77	

<sup>a</sup>Spectra measured at 100 K in CDCl<sub>3</sub>-DMF- $d_7$  solutions prepared in nonanhydrous conditions. <sup>b</sup>n m = not measured. <sup>c</sup>Other lines, not assigned, but due to the presence of water, show splittings of 2.39 and 1.88 MHz (|| and  $\perp$  ENDOR, respectively).

extrema of the magnetic interaction measured in the molecular xy plane.

In spite of the larger number of lines an approach similar to that detailed before for the parallel spectra has allowed complete assignment of the spectra of VO(acen) and VO(salen). The results of this analysis are summarized in Tables II and III.

As an example we outline below the line assignment procedure followed for the key compound VO(salen).

The lines due to the axial and equatorial ethylenediamine were identified by comparing the spectrum of VO(acen) with the results reported for VO(acac)<sub>2</sub>.<sup>8</sup> As expected a total of four line pairs were found, corresponding to the y (the two largest) and x (the two smallest) components of the hyperfine tensors of the two sets of inequivalent protons.

As already pointed out for the parallel spectra, these lines show only minor changes on going from VO(acen) to the salen-type complexes and are easy to identify for most of the spectra presented in Figure 4. Only in a few cases complete determination of the splittings was hampered by broadening or superposition of lines.

The largely different metal proton distances displayed by the axial and equatorial protons allow immediate assignment of the experimental data. After tensor transformation (see below) the anisotropic parts of the hyperfine tensors due to the axial and equatorial protons are quite close to those reported for the related Cu(salen).<sup>26</sup> This finding strongly supports the correctness of our analysis.

Assignment of the other lines in the perpendicular ENDOR spectrum of VO(salen) was generally confirmed by comparison with the spectra of the complexes containing the properly substituted ligands. This is the case for protons  $H_7$ ,  $H_3$ , and  $H_5$ . The spectra of VO(salen) and VO(3-CH<sub>3</sub>Osalen) show that the pair of lines split by ca. 1.0 MHz sums two different contributions. One is, of course, the smaller in-plane (x) component of the  $H_3$ coupling tensor, whereas the second has been ascribed to the largest in-plane (y) component of the  $H_6$  coupling tensor. In the spectrum of VO(salen) the lines of these latter protons are the only ones which have been assigned without direct experimental proof but simply on the basis of satisfactory agreement with the dipolar model.

Finally it is worth noting that in both the parallel and perpendicular spectra we could not find any evidence for lines due to the H<sub>4</sub> protons, whereas the two smaller components of the hyperfine tensor of the more distant H<sub>5</sub> protons could be unequivocally located. The third one, i.e., the largest, expected to be ca. 0.5 MHz, could not be assigned with certainty and is probably buried under the H<sub>6</sub> lines of the perpendicular spectrum.

Again the spectra of VO(salphen) and VO(3-CH<sub>3</sub>Osalphen) show much lower resolution, in this case essentially due to the

TABLE V: Proton Hyperfine Coupling Parameters after Tensor Transformation (MHz) and Spectroscopic and Crystallographic V-H Distances (pm) and H-V-O Angles (deg)<sup>a,b</sup>

		ENDOR					X-ray		
proton	$A_{\parallel}$	$A_{\perp}$	A <sub>iso</sub>	A <sub>dip</sub>	r	v	r	θ	
H3	2.03	-1.01		2.03	427	90 ± 7	438	98	
$H_7$	3.21	-1.51	0.06	3.15	370	90 ± 14	385	100	
H <sub>6</sub>	1.01	-0.47	0.02	1.03	535	90	528	89	
H <sub>5</sub>	0.52	-0.26		0.52	662		651	97	
H <sub>ax</sub>	4.74	-2.51	-0.09	4.81	320	$90 \pm 12$			
H <sub>eq</sub>	4.03	-2.11	-0.06	4.09	338	90 ± 13			
Hax	5.09	-2.84	-0.20	5.29	310	90 ± 8	305	79	
Hear	3.91	-2.11	-0.10	4.01	340	90 ± 19	324	108	
-1							380	96	
$H_2O^d$	6.0	-2.77	0.15	5.85	300		290		

<sup>a</sup>X-ray data are taken from the crystal structures of VO(acen),<sup>30</sup> FeNO(salen),<sup>25</sup> and Mg(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>.<sup>33,34</sup> <sup>b</sup>Unless otherwise stated reported data refer to VO(salen). The other salen-type complexes display very similar coupling parameters. <sup>c</sup>VO(acen). <sup>d</sup>VO(3-CH<sub>3</sub>Osalphen).

much larger density of the spectral lines, so that only incomplete assignment of these spectra was possible. Table IV shows that complete results were obtained only for protons in position 3, whereas only some tensor components could be measured for the protons  $H_6$ ,  $H_7$ , and  $H_9$ . Besides, lines due to water protons were identified also in these spectra and ascribed to the presence of axially bound water. In addition the spectrum of VO(3-CH<sub>3</sub>Osalphen) shows also lines tentatively assigned to water proton hydrogen bound to the vanadyl oxygen.

#### Discussion

The above results show that simple analysis of the frozen solution ENDOR spectra of a series of structurally related compounds may yield the full hyperfine interactions (in terms of the three magnetic components along the **g** or metal hyperfine tensor axes) of several protons, even in rather complicated systems.

Perhaps it is useful to recall that frozen solution ENDOR spectra in fully deuterated solvents completely eliminate the presence of strong matrix ENDOR lines close to the free proton esonance and due to surrounding magnetic nuclei. This means that, as far as the more distant protons of our molecule are concerned, the frozen solution technique offers a resolution which is not easily paralleled by solid-state, powder or single-crystal spectra.

In principle this large amount of data may provide access to structural information not readily obtainable in a different way. The main problem is that the experimental values are measured in the g-axes reference frame. Therefore, generally speaking, they are not principal values of the magnetic interactions. However, Figure 6 shows that in the case of axial or quasi-axial symmetry a single rotation angle,  $\vartheta$ , relates the two sets of principal axes. Rotation occurs around the x' axis, which lies in the xy plane. In other words one of the experimental hfs values obtained from the  $\perp$  ENDOR spectrum (the smaller) is a principal value, whereas the other two, obtained respectively from the || and  $\perp$ ENDOR, are not. Tensor transformation is required and, if we assume the point dipole approximation to be valid (i.e., the proton hfs tensors to be axially symmetric), and estimate of the rotation angle may be obtained.

The rotation formulas derived by Hoffman et al.<sup>10</sup> have been used and are reported below since, due to a misprint, a  $2^{1/2}$  factor has been omitted in ref 10

$$A_{x'} = A_x \tag{1}$$

$$A_{y'} = \left[ \frac{A_{y'}^2 - (A_{y'}^2 + A_{z'}^2)\sin^2\vartheta}{1 - 2\sin^2\vartheta} \right]^{1/2}$$
(2)

$$A_{z'} = \left[ \frac{A_{z}^{2} - (A_{y}^{2} + A_{z}^{2})\sin^{2}\vartheta}{1 - 2\sin^{2}\vartheta} \right]^{1/2}$$
(3)

The assumption of axial symmetry gives the additional condition

L

$$A_{x'}| = |A_{z'}| \tag{4}$$



Figure 6. Sketch of the general orientation of the principal axis system for g and proton hyperfine tensors.

 $A_i$  and  $A_{i'}$  are the experimental and rotated tensor components. From eq 1-4 we obtain the angle between the metal proton direction and the reference axis represented by the vanadyl bond. Furthermore, the hfs principal values can be derived. Their average gives the isotropic components, whereas the anisotropic parts may be used to derive the metal proton distances according to the simple dipole formula.<sup>27</sup>

$$A_{\rm D} = A_{\rm y'} - A_{\rm iso} = \mu_{\rm b} \mu_{\rm n} g_{\rm e} g_{\rm n} (3 \cos^2 \alpha - 1) / r^3$$

Table V summarizes some of the results of this analysis and allows the validity of the point dipole approximation to be verified.<sup>28</sup> However, before we proceed there are some ambiguities in our approach which need to be clarified.

Derivation of the isotropic and anisotropic couplings from the experimental data requires knowledge of the relative signs of the tensor components. This information is usually not available and would require triple resonance experiments to be performed.<sup>29</sup> In the past attempts have been made to obtain the relative signs by measuring the hyperfine splittings as a function of  $B_0$ ,<sup>23</sup> but later on this approach has been shown to be misleading.<sup>8</sup> However, the choice of the VO(II) ion as paramagnetic probe considerably simplifies the problem since, in the case of this  $\sigma$  nonbonding ion, sizeable isotropic contributions are possible only for very close, properly oriented protons.<sup>22</sup> Generally speaking the magnetic interaction is dominated by its dipolar part and this makes the sign choice trivial. In our case different possibilities invariably lead to unrealistically large isotropic terms and small dipolar components.

(29) Biehl, L.; Plato, M.; Mobius, K. J. Chem. Phys. 1975, 63, 3515.

<sup>(27)</sup> Schweiger, A.; Rist, G.; Gunthard, Hs. H. Chem. Phys. Lett. 1975, 31, 48.

<sup>(28)</sup> One of the referees has suggested that, in an essentially dipolar interaction, the anisotropy of the electron magnetic moment, due to the g tensor anisotropy, should be taken into account as indicated by Hutchison.<sup>36</sup> However, in this case the g anisotropy is small and numerically not significant. For this reason its effect has not been included in eq 1-4.

Another point is the possibility of error propagation from the calculated value of  $\vartheta$  to the calculated value of r. In spite of the results of Table V we may assume that our  $\vartheta$  values are rather crude estimates of the real ones. However, it is easy to show that the value of the rotation angle affects only the isotropic part of the tensors, whereas it leaves completely unaffected the dipolar component  $A_{y'} - A_{iso}$ . This means that our calculated r values do not depend upon the tensor transformation we perform.

The final point we want to stress is the ambiguity in the derivation of  $\vartheta$ . The rotation angle enters eq 1-3 as a squared sine function. This means that we can easily derive its absolute value but we cannot discriminate between clockwise and anticlockwise rotations. Although reasonable guesses can often be made this appears to be the major drawback of this kind of analysis.

Table V reports the tensor principal values together with the geometrical parameters  $\vartheta$  and r. Literature X-ray data are also included for comparison. Unfortunately very few crystal and molecular structures of relevant VO(II) complexes have been published and only rarely do standard X-ray reports include hydrogen coordinates at least in fixed ideal positions. However, besides the X-ray work on VO(acen),<sup>30</sup> careful examination of the existing literature suggests that the X-ray structures of FeNO(salen)<sup>25</sup> and Co(3-CH<sub>3</sub>Osalen)(H<sub>2</sub>O)<sup>31</sup> can be used with some confidence to test the spectroscopic information obtained from the vanadyl salen-type complexes.

As far as the aromatic ring protons are concerned complete data are presented for protons  $H_3$ ,  $H_6$ , and  $H_7$ , whereas only partial results are available for the more distant  $H_5$  proton. In this case only one perpendicualr hyperfine value,  $A_z$ , could be measured with certainty and an estimate for *r* was obtained simply assuming this component to be a principal value with negligible isotropic contribution. Keeping in mind the rather crude approximations used, the results of Table V appear to be quite satisfactory. Particularly instructive is the comparison with the results obtained by Schweiger et al.<sup>32</sup> and Iwaizumi et al.<sup>26</sup> with detailed singlecrystal studies of the related Cu-doped compounds bis(salicylaldoximato)nickel(II) and N,N'-ethylenebis(salicylaldhydeiminato)nickel(II).

It turns out that the experiments with unoriented vanadyl compounds, performed at high temperature (>100 K), provide structural information of comparable accuracy and in some cases, i.e., the more distant  $H_5$  and  $H_6$  protons, they allow the resolution of lines which could not be detected in the single-crystal work. Furthermore, whenever the metal proton distance is large enough to allow the point dipole approximation to be valid for both metal ions, the results indicate that both Cu(II) and VO(II) behave as pure paramagnetic probes. A striking example is the magnetic coupling of proton H<sub>3</sub> which gives distances of 421, 429, and 427 pm respectively, for Cu(salen), Cu(salox)<sub>2</sub>, and VO(salen). The conclusion is that, as far as structural data are concerned, the use of copper simply implies the presence of additional problems, namely short relaxation times, large isotropic contributions, and the breakdown of the point dipole approximation at distances which are about 15 pm larger than for VO(II).

The couplings of the ethylenediamine bridge protons require some further comment. In the case of VO(acen) the axial protons give rise to a single set of lines with corresponding r and  $\vartheta$  values of 309 pm and 82°. The X-ray results for the two slightly inequivalent axial protons are 304 and 305 pm with rotation angles 74° and 84° (average 79°).<sup>28</sup> The situation is different for the two equatorial protons which are found, in the X-ray structure, at the largely different distances 324 and 380 pm. Apparently this is the result of a bridge conformation intermediate between gauche and eclipsed. The torsion angle around the carbon-carbon bond is 33°, whereas the expected values for the two limiting cases are 60° and 0°. In spite of this the ENDOR results again suggest a single set of lines which analyzed as usual to give r = 340 pm and  $\vartheta = 109^\circ$ . A possible explanation is that VO(acen) in solution assumes the more usual eclipsed conformation. This would explain the spectroscopic equivalence of the two protons and also the intermediate value of their distance. However, the distance calculated for the axial protons does not reflect this conformational change. Therefore the possibility that we failed to detect a second set of lines, due to the more distant equatorial proton, cannot be excluded. The situation is similar in the salen-type complexes, but in this case thermal disorder of the bridge prevents comparison with crystallographic data.<sup>31</sup>

Finally the proton coupling of the water molecule axially coordinated to VO(salphen) and VO(3-CH<sub>3</sub>Osalphen) is very similar to the values already reported in the literature<sup>20,22</sup> and leaves little doubt on the identification of these lines. The point is that these data could not give any orientational information and this is directly related to the axial coordination of the water ligand. Figure 6 clearly shows that in this case the largest hfs component is obtained from the parallel ENDOR spectrum, whereas the perpendicular one should yield the two smaller couplings  $A_x$  and  $A_{v}$ . Of course the anisotropy in this plane is very small, simply being, in our approximation, the result of a nonzero  $\vartheta$  value. Therefore resolution of the two couplings, which in the preceding examples could be measured precisely and independently in the two different ENDOR orientations, is not possible. The result is an apparently axial coupling tensor (or zero  $\vartheta$  value) which points to a metal proton distance of 300 pm against a value of 290 pm reported for  $[VO(H_2O)]_5^{2+,22,33,34}$  This difference, probably due to the steric hindrance of the bulky organic ligands, is by no means negligible. At such short distances it corresponds to a difference in the dipolar coupling of about 0.5 MHz.

## Conclusions

The results discussed above indicate that the possibility of using ENDOR as a current spectroscopic technique for obtaining structural information in terms both of distances and angles depends primarily on a suitable choice of the metal ion to use as the paramagnetic probe.

From this point of view, two different aspects must be stressed, i.e., the spatial distribution of the unpaired electron and the relaxation properties of the metal ion. The lanthanides offer, of course, the highest localization of the unpaired electron but have the great disadvantage that very low temperatures, around 2 K, are necessary to measure their spectra.<sup>35,36</sup> Apparently the VO(II) ion offers a better compromise in that it gives good spectra at temperatures higher than 100 K and has the correct ground state to minimize the spread of its unpaired d electron.

As far as resolution is concerned we have already noted that, due to the absence of matrix lines, the frozen solution technique offers the best opportunity to measure weakly coupled protons.

With respect to single-crystal measurements the measured magnetic parameters are, of course, much less accurate. However, since the derivation of structural data always depends on some kind of dipolar approximation the final results may be of comparable accuracy.

In conclusion rigid matrix ENDOR spectra appear to provide a wealth of information with a rather limited experimental effort and they seem particularly suited for the characterization of systems which contain paramagnetic ions or complexes bound to complex inorganic or organic matrices.

**Registry** No. VO(acen), 19195-97-2; VO(salen), 36913-44-7; VO(3-CH<sub>3</sub>Osalen), 82405-41-2; VO(5-Cl-salen), 32065-14-8; VO(7-CH<sub>3</sub>salen), 22785-42-8; VO(salphen), 32065-17-1; VO(3-CH<sub>3</sub>Osalen), 98774-89-1.

<sup>(30)</sup> Bruins, D.; Weaver, D. L. Inorg. Chem. 1970, 9, 130.

<sup>(31)</sup> Calligaris, M.; Nardin, G.; Randaccio, L. J. Chem. Soc. Dalton Trans. 1974, 1903.

<sup>(32)</sup> Schweiger, A.; Gunthard, Hs. H. Chem. Phys. 1978, 32. 35.

<sup>(33)</sup> Margulis, T. N.; Templeton, D. H. Z. Kristallogr. 1962, 117, 344.
(34) Brown, G. M.; Chidambaram R. Acta Crystallogr. Sect. B 1969, 25, 676.

<sup>(35)</sup> Hutchinson, Jr., C. A.; McKay, D. B. J. Chem. Phys. 1977, 66, 3311.
(36) Hutchinson, Jr., C. A.; Orlowski, T. E. J. Chem. Phys. 1980, 73, 1.