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Vanadyl metal mesogen derivatives: an EPR study

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Abstract. An EPR study of the metallo-organic compounds *bis*[*N*-pentyl, 4-(4-decyloxybenzoyloxy) salicylaldiminato] of oxovanadium (IV) and *bis*[*N*-(4-pentyloxyphenyl), 4-(4-decyloxybenzoyloxy) salicylaldiminato] of oxovanadium (IV) is presented. Both materials are mesogenic and undergo some phase transitions between room temperature and 150 °C (for the first compound) and 270 °C (for the second one). The EPR signals are due to the vanadyl group. The spectra have been measured at different temperatures and the changes in them have been correlated with some of the phase transitions. Modifications in the spectra occurring after several heating–cooling cycles dependent on the presence or absence of an applied magnetic field (up to 1.4 mT) are also observed. The behaviour is discussed in terms of molecular orientations in the presence of a magnetic field. A qualitative discussion of the different contributions to the magnetic susceptibility is given.

1. Introduction

A noticeable and useful characteristic of liquid crystals is that they can achieve a long-range orientational molecular order in the presence of either electric or magnetic fields [1, 2]. Because of this property liquid crystals have been widely used as solvents in a great number of studies, as well as in many applications where it is necessary to obtain molecular orientation of other substances. With that aim, liquid crystals have been used in NMR [3], EPR [4] and Mössbauer [5] spectroscopies as well as in other techniques such as gas chromatography [6].

On the other hand the synthesis of mesomorphic transition metal complexes has greatly improved in recent years because of the special combination of liquid crystal properties with a transition metal in the structure of the molecule [7, 8]. In these compounds the properties of the liquid crystal solvent and the substrate are added to the same molecule, and then interesting new properties are observed [9, 10]. Moreover, the choice of the correct metal ion can introduce unusual electro-optical and magnetic properties that make these materials potentially very useful for several applications [11, 12]. These compounds could also be of interest as a means of controlling molecular orientation with respect to an applied magnetic field by introducing suitable paramagnetic units in polymeric chains [13] or in mixtures [14, 15].

With these ideas in mind we present in this paper an EPR study of two mesogen complex vanadyl derivatives: *bis*[*N*-pentyl, 4-(4-decyloxybenzoyloxy) salicylaldiminato] of oxovanadium (IV), hereafter named V5 for brevity, and *bis*[*N*-(4-pentyloxyphenyl),4-(4-decyloxybenzoyloxy) salicylaldiminato] of oxovanadium (IV), hereafter VO5. These compounds exhibit nematic mesophases at relatively low temperatures. Moreover their low viscosity in the mesophase makes them potentially orientable in a magnetic field. Our studies confirm this guess, indicating the usefulness of these materials for the above-cited applications. Besides structural information on vanadyl ions, our data permit us to analyse qualitatively the different contributions to the anisotropy of the magnetic susceptibility, and then to discuss the difference in the behaviour of these materials with respect to their orientation in a magnetic field as compared with divalent copper counterparts [16].

2. Experimental procedure

V5 and VO5 compounds were synthesized in our Institute following a procedure outlined elsewhere [17]. The products obtained were characterized by microanalysis with fairly good results.

The stability of the complexes was studied by thermogravimetric analysis under nitrogen using a Perkin–Elmer TGS-2 equipped with a system 4-microprocessor using a 10 °C min^{-1} heating rate. None of them showed weight loss up to 274 °C or higher temperatures, confirming the absence of water molecules in these compounds.

The phase behaviour was examined, using polarizing light, with an optical microscope equipped with a Mettler FP82 hot stage and a Mettler FP80 microprocessor.

Measurements of the phase transition temperatures (T_t) and enthalpies (ΔH) were made using a Perkin–Elmer DSC-2 differential scanning calorimeter with a 10 °C min^{-1} heating rate. The apparatus was calibrated using indium (156.6 °C, 28.4 J g^{-1}) and tin (232.1 °C, 60.5 J g^{-1}) as standards.

The EPR spectra were measured with a Varian E-122 spectrometer working in the X-band. For measurements above room temperature (RT) the variable-temperature accessory (E-265) from Varian was used. The powdered samples were placed inside a quartz tube and the temperature was monitored using a copper–constantan thermocouple attached to the tube. The error in temperature was estimated to be lower than 0.5 °C and the stability better than 0.1 °C.

3. Experimental results

Both complexes are mesogens and their mesophases were identified by their optical texture. The temperatures and enthalpies of the transitions are collected together in table 1. It is noticeable that the VO5 compounds exhibit an additional birefringent phase, which is stable between 174 °C and 225 °C; but in some experiments their gum-like behaviour under mechanical stress indicate that they are not crystalline [17]. It is a kind of *special smectic* phase, which has been labelled S_{crys}, and has been characterized in [17].

At RT the EPR spectra of both V5 and VO5 compounds show a complex signal centred at $g \simeq 2$, being extended by about 0.16 T. These spectra have also been measured at different temperatures between RT and 150 °C and 250 °C for V5 and VO5 respectively. These measurements have been performed before and after several heating–cooling cycles, either in the presence or in the absence of a strong magnetic field (up to 1.4 T).

In figure 1 we show the spectra of a V5 sample taken at RT before any treatment (*a*) and after heating up to 150 °C (*isotropic liquid* phase), followed by a subsequent *slow* cooling down to RT in the absence of any magnetic field (*b*). This last signal is simpler

Table 1. Temperatures (T_t) and enthalpies (ΔH) of the different phase transitions of the V5 and VO5 compounds. (S: solid crystal phase; N: nematic phase; S_{crys}: a kind of smetic phase (see the text); I: isotropic liquid phase.)

Compound	Transition type	T_t (°C)	ΔH (kJ mol^{-1})
V5	$C \rightarrow N$	109.4	89.86
	$N \rightarrow I$	131.0	4.88
VO5	$C \rightarrow S_{crys}$	173.9	35.65
	$S_{crys} \rightarrow N$	224.8	29.78
	$N \rightarrow I$	266.5	1.06

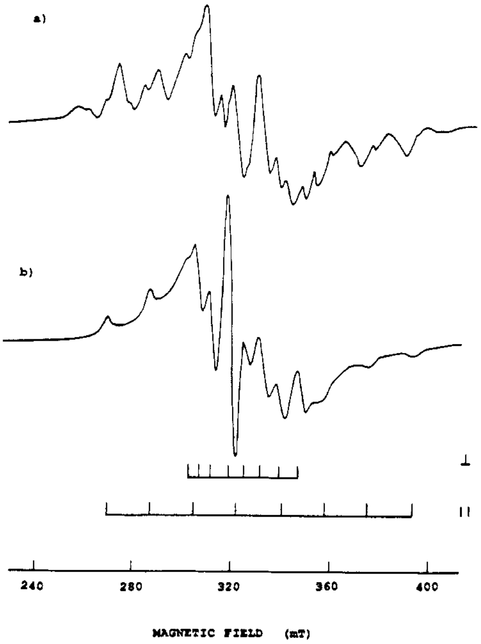

Figure 1. EPR spectra measured at RT of a V5 powder sample (*a*) just after synthesizing it and (*b*) after subsequent heating up to 150 °C (*isotropic liquid* phase) and then cooling down to RT without any applied magnetic field.

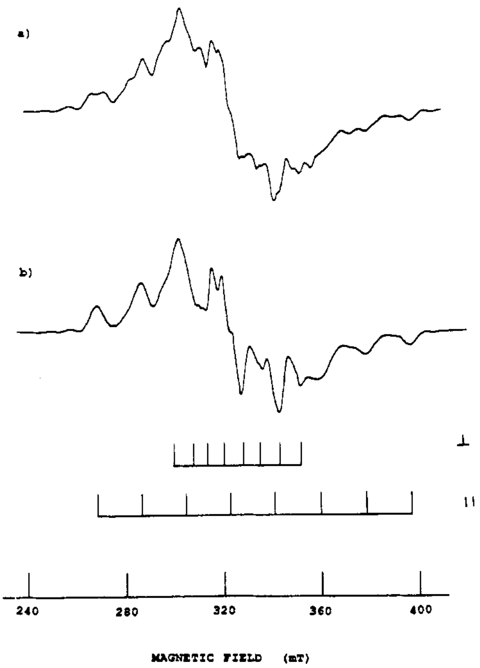

Figure 2. EPR spectra measured at RT of a VO5 powder sample (*a*) just after synthesizing it and (*b*) after subsequent heating up to 250 °C (*nematic* phase) and then cooling down to RT without any applied magnetic field.

and presents, among other lines, four features (two on each side) having a *parallel* character. Hereafter, it will be labelled I. Taking into account the separation between two adjacent peaks (about 18 mT) and the total splitting, these four parallel signals can be considered as a part of a set of eight uniformly spaced parallel signals, which correspond to the hyperfine structure due to the interaction of the unpaired 3d electron with the ^{51}V nucleus ($I = \frac{7}{2}$, 100% natural abundance). In the central region of the spectrum the other four parallel signals overlap with the eight perpendicular ones, which show a smaller splitting. This spectrum is typical for tetravalent vanadium, either isolated or forming part of a vanadyl $(VO)^{2+}$ molecular ion in powdered as well as glassy samples [18–23], so it will be associated with the $(VO)^{2+}$ group in our molecule.

In a similar way the spectrum of an untreated sample (see figure 1(*a*)) can be explained. In that case at least four clearly resolved different $(VO)^{2+}$ signals are distinguished among the parallel features. Upon subsequent heating and cooling cycles in the absence of a magnetic field the observed spectrum does not vary from that given in figure 1(*b*).

In figure 2 the results corresponding to the VO5 sample are depicted. In this case the *simplest* spectrum is obtained by heating up to 250 °C (nematic phase) and then cooling the sample down to RT without any applied magnetic field as in the previous case. Further heating and cooling treatments give rise to the same spectrum. Again the dominant signal that appears in the treated samples (see figure 2(*b*)) will be labelled I.

Changes in the EPR spectra of both compounds are also observed when measured at higher temperatures. The observed modifications are correlated with the phase transitions (table 1).

In the case of V5 compound no changes are observed in its EPR spectrum if the sample is either in the solid or in the nematic phase, but some modifications of the spectrum can be observed when our sample is in the isotropic liquid phase. This behaviour is independent of the previous thermal treatment. In figure 3 we show the EPR spectrum of a V5 sample in the isotropic liquid phase measured at 140 °C (figure 3(*a*)) and at 150 °C (figure 3(*b*)). In the former it can been seen that the parallel spectrum has almost disappeared, while at 150 °C these features are detected again but their intensities as compared with those of the perpendicular signals are lower than in the RT phase (see figure 1(*b*)).

As has been said above, when a sample heated to 150 °C is cooled down to RT without applying any magnetic field, its EPR spectrum coincides with that shown in figure 1(*b*). Different results are obtained when the sample is cooled down to RT in the presence of a magnetic field $\boldsymbol{B}_0$ (of about 1.4 T). We show in figure 4 the EPR spectra measured at 115 °C (nematic phase) with the DC magnetic field parallel to $\boldsymbol{B}_0$ (*a*), and at RT (solid phase) with the DC magnetic field either parallel (*b*) or perpendicular (*c*) to $\boldsymbol{B}_0$. If the DC magnetic field is parallel to $\boldsymbol{B}_0$, only the perpendicular signal is observed, but if the sample is rotated 90° at RT (DC magnetic field perpendicular to $\boldsymbol{B}_0$) its spectrum shows both the parallel and perpendicular features, but their relative intensities change with respect to those observed in figure 1(*b*) in such a way that the parallel ones increase proportionally.

In the case of the VO5 compound, modifications of its EPR spectrum are also observed when it is measured in different phases. In figure 5 we show the EPR spectra taken at 190 °C (S_{crys} phase; figure 5(*a*)) and at 250 °C (nematic phase; figure 5(*b*)). When the sample is cooled down to RT the same spectrum as that shown in figure 2(*b*) is observed regardless of whether the cooling process has been performed with or without a strong magnetic field, and no modifications are observed when the sample is rotated in the magnetic field at RT.

4. Discussion

As has been said above, the EPR signals observed in the V5 and VO5 EPR spectra can be associated with the $(VO)^{2+}$ group. Taking into account the different spectra measured at RT (mainly those given in figures 1(*b*), 4(*b*) and 4(*c*) for V5 and in figures 2(*b*) and 5(*b*)

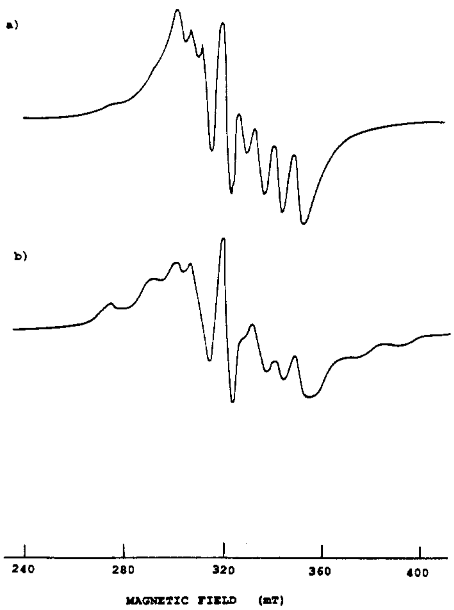

Figure 3. EPR spectra of a V5 sample measured in the *isotropic liquid* phase at 140 °C (*a*) and at 150 °C (*b*).

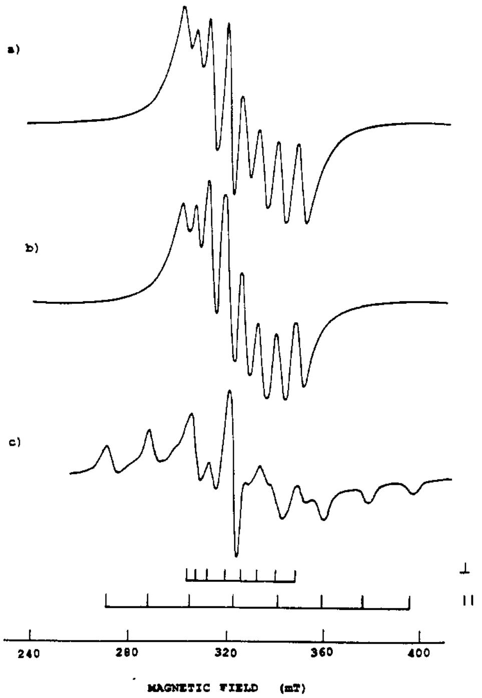

Figure 4. EPR spectra of a V5 sample heated up to 150 °C and then cooled in the presence of a magnetic field $\boldsymbol{B}_0$ of about 1.4 T down to the measurement temperature: 115 °C (*nematic* phase) with the DC magnetic field parallel to $\boldsymbol{B}_0$ (*a*) and RT with the DC magnetic field either parallel (*b*) or perpendicular (*c*) to $\boldsymbol{B}_0$.

for VO5), the EPR spectrum of $(VO)^{2+}$ in our thermally treated samples (type I signals) can be explained using the following axial spin Hamiltonian:

$$\mathcal{H} = \mu_B[g_\perp(S_xB_x + S_yB_y) + g_\parallel S_zB_z] + A_\perp(S_xI_x + S_yI_y) + A_\parallel S_zI_z \quad (1)$$

where $S = \frac{1}{2}$ and $I = \frac{7}{2}$, μ_B is the Bohr magneton, and $g_\perp$, $g_\parallel$, $A_\perp$ and $A_\parallel$ have their usual meanings. A fitting of the predicted resonance field using equation (1) to the experimental fields yields for the spin-Hamiltonian parameters the values depicted in table 2. With these values and using the former spin Hamiltonian the parallel and perpendicular features have been calculated. They are shown by the stick diagram in the figures. As can be seen, the hyperfine coupling tensor shows a strong anisotropy as is usual for the d electron in the $(VO)^{2+}$ molecular ion [18–24]. On the other hand it is found that $g_\parallel < g_\perp < g_e$.

The outermost electronic configuration of the $(VO)^{2+}$ ion consists of an unpaired 3d electron ($3d^1$). When this ion is part of a molecule in such a way that its point symmetry is lower than that of the free ion, the fivefold degeneracy of the $3d^1$ is removed. In spite of the lack of any point symmetry operations in our molecules the neighbourhood of $(VO)^{2+}$ can be approximately described as a perturbed planar square symmetry [17]. In such a situation the ground state of the unpaired electron can be approximately described

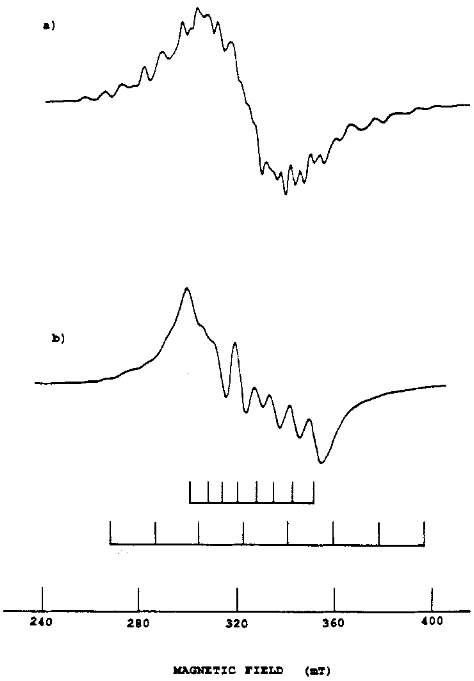

Figure 5. EPR spectra of a VO5 sample measured at 190 °C (S_{crys} phase) and at 245 °C (*nematic* phase).

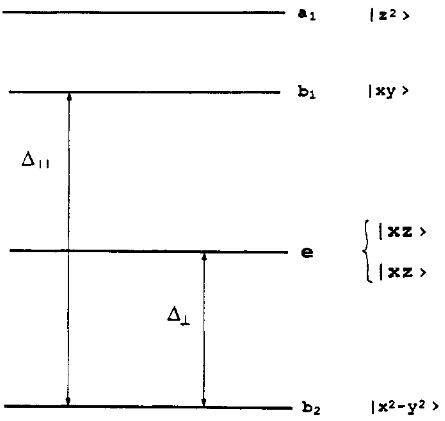

Figure 6. Energy levels for a d electron in a square planar environment (C_{4v} point symmetry).

Table 2. Spin-Hamiltonian parameters for the $(VO)^{2+}$ paramagnetic entities in V5 and VO5 compounds. The hyperfine constants are given in MHz. The estimated error for the g-factors is ±0.005 and for the hyperfine constant ±5 MHz.

Compound	Centre	$g_\parallel$	$g_\perp$	$A_\parallel$	$A_\perp$
V5	I	1.945	1.980	485	180
	II	1.950	—	580	—
	III	1.945	—	555	—
	IV	1.950	—	450	—
VO5	I	1.940	1.970	500	190
	II	1.940	1.970	575	225

as a $|x^2 - y^2\rangle$ wavefunction [25]. Then, and up to a second-order perturbation, within the frame of a ligand field theory the principal values of the g-tensor are given by [26]

$$g_\parallel = g_e - 8\lambda\alpha^2/\Delta_\parallel \qquad g_\perp = g_e - 2\lambda\alpha^2/\Delta_\perp \tag{2}$$

where the meaning of $\Delta_\parallel$ and $\Delta_\perp$ is given in figure 6 and α is the coefficient of the metal $d_{x^2-y^2}$ orbital in the ground state $|x^2 - y^2\rangle$ wavefunction within a molecular orbital description. In such a situation it follows that $g_\parallel < g_\perp < g_e$, as is observed. Within the same theoretical framework the principal values of the hyperfine tensor are given [26] as

$$A_{\parallel} = -P[\kappa + \tfrac{4}{7}\alpha^2 + (g_e - g_{\parallel}) + \tfrac{3}{7}(g_e - g_{\perp})] \qquad A_{\perp} = -P[\kappa - \tfrac{2}{7}\alpha^2 + \tfrac{11}{14}(g_e - g_{\perp})] \tag{3}$$

where $P = g_e g_N \mu_B \mu_N \langle r^{-3} \rangle_d$ and g_N is the nuclear g-factor. κ accounts for the contact isotropic contribution to the hyperfine interaction and is related to the spin density at the ^{51}V nucleus given by

$$\chi = -\tfrac{3}{2}\kappa \langle r^{-3} \rangle_d . \tag{4}$$

Using the Hartree–Fock radial function calculated by Clementi and Roetti [27] for the tetravalent vanadium ion, we obtain $\langle r^{-3} \rangle_d = 3.67$ au, and with $g_N = 1.408$ we obtain for P a value of 515 MHz. Then using the values obtained above for the spin-Hamiltonian parameters we estimate that the spin density χ at the vanadium nucleus to take the values 2.82 au and 2.85 au for type I $(VO)^{2+}$ in V5 and VO5 respectively. These values are in the range of those reported in the literature for the vanadyl ion [21, 22, 24].

From equation (3) we estimate a value of 0.75 for the coefficient of the central-ion wavefunction in the molecular orbital. Although this value indicates that the approximations underlying the formulation given by equations (2) and (3) are doubtful in our case, we continue to use them. Thus this value deviates noticeably from unity, indicating that there is an important contribution from the ligand orbital to the unpaired wavefunction. In such a situation the principal hyperfine values (and also the principal g-values) are expected to be strongly dependent on the chemical bond with the first neighbours, owing to the orbital contribution to the hyperfine constants determined by the covalent effects.

With these ideas the complex spectrum of untreated V5 samples (see figure 1(*a*)) can also be easily understood. It is well known that for this type of material, when prepared following the chemical procedure given above, a polymorphic sample is obtained [28]. In such samples various environments for the vanadyl ion coexist and the different traces, which appear clearly resolved for the parallel features, can be associated with these $(VO)^{2+}$ environments (labelled II, III and IV in table 2). An estimate of the parallel components of the g- and hyperfine tensors of these unstable $(VO)^{2+}$ environments from the spectrum in figure 1(*a*) gives the values in table 2. When the sample is heated up to the isotropic liquid phase and then slowly cooled down to RT the less energetic phase is mainly formed at the expense of the other allotropic ones; then a simpler spectrum, as shown in figure 1(*b*), is observed.

As seen from figure 2, the VO5 compound behaves similarly. In this case the isotropic liquid phase has not been reached, because of a partial decomposition, but the more stable type I $(VO)^{2+}$ environment is obtained after thermal annealing in the nematic phase. A small contribution from another $(VO)^{2+}$ centre (type II) is observed in the RT spectra of thermally annealed samples (see figure 2(*b*)). An estimate of its spin-Hamiltonian parameters is also given in table 2.

Now we comment on the differences found in the EPR spectra when the samples are cooled down to RT from the isotropic liquid phase in the presence of a magnetic field $\boldsymbol{B}_0$.

X-ray diffraction measurements in the presence of a magnetic field show that in the isotropic liquid phase the V5 molecules, which are able to rotate, are oriented in such a

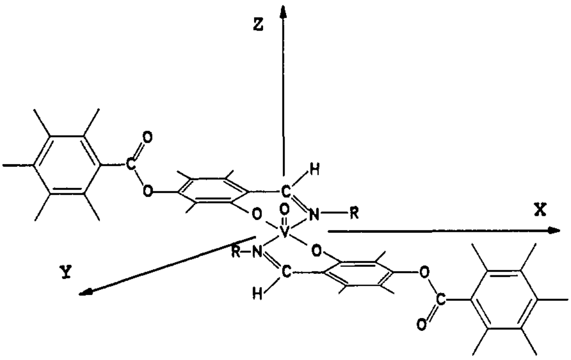

Figure 7. A schematic model for the V5 and VO5 molecules showing the coordinated system used in the text. R = $-C_5H_{11}$ (V5) and R = $-(C_6H_4)-C_5H_{11}$ (VO5).

way that their axes (the x axis in figure 7) are parallel to $\boldsymbol{B}_0$ and then all the $(VO)^{2+}$ have their z axes perpendicular to $\boldsymbol{B}_0$. This explains the spectrum given in figure 3(*a*). The measuring field orients the molecules and only the perpendicular signal is observed. If the temperature is increased, in the isotropic liquid phase the thermal agitation works against the magnetic interaction that tends to orient the molecules. That explains the increase in strength of the parallel signal in the spectrum given in figure 3(*b*).

When the sample is cooled down to RT in the magnetic field, the orientation of the V5 molecules is unchanged, because they are not able to move freely in the low-temperature phases. According to the EPR spectrum measured with the DC magnetic field, $\boldsymbol{B}_m$, parallel to $\boldsymbol{B}_0$, only the perpendicular signal is detected in either the nematic or the solid phase (see figures 5(*a*) and 5(*b*)). A uniform distribution for the orientation of the y and z axes in the plane perpendicular to the x axis is reached. Now, if the magnetic field is rotated by 90° it will be directed along a random direction in the yz plane. Then the probability of the angle θ that the magnetic field makes with the z axis taking a value between θ and $\theta + d\theta$ is given by

$$f_\perp(\theta)\,d\theta = (1/\pi)\,d\theta \qquad (0 \leqslant \theta \leqslant \pi) \tag{5}$$

instead of

$$f_0(\theta)\,d\theta = \tfrac{1}{2}\sin\theta\,d\theta \qquad (0 \leqslant \theta \leqslant \pi) \tag{6}$$

which gives the corresponding probability in the case of a free random orientation in the whole space [29]. Thus it is clear why the parallel signal increases as compared with the perpendicular one, as seen when the spectra given in figures 1(*b*) and 3(*c*) are compared.

The orientation of the V5 molecules in the presence of a magnetic field is due to the anisotropy of the molecular magnetic susceptibility tensor χ_m. In the case of metallo-organic compounds—like the present one—there are two main contributions to the anisotropy of χ_m: the contribution of the paramagnetic entity due to the anisotropy of its g-tensor and the strong anisotropic diamagnetic susceptibility of the benzene rings. A combination of these is responsible for the actual orientation of the whole molecule in the presence of a magnetic field. In our case the g-factor values (see table 2) show that the anisotropy of the paramagnetic contribution is small, and such that it favours the V–O bond being perpendicular to the magnetic field; that is, the molecules orientate with the magnetic field in the xy plane. It is also known that the benzene rings orientate tending to keep the magnetic field in the ring plane [30]. Since, in our V5 molecule, benzene rings are placed in two planes that intersect along the x axis, the anisotropy in the diamagnetic contribution also favours the molecule being oriented with the magnetic field directed along its x axis (see figure 7). This is consistent with the x-ray diffraction data and with our EPR results.

It would be interesting to compare our results with those for the homologous copper complex [17] (Cu5), where magnetic-field-induced EPR anisotropy was not observed because the higher anisotropy of the g-tensor [17] gives a strong anisotropic paramagnetic contribution to χ_m. X-ray diffraction experiments on Cu5 in the high-temperature phases show that the Cu5 molecule orientates mainly perpendicularly to the magnetic field, so the paramagnetic contribution is the dominant one in this case. Nevertheless, the EPR experiments in [16] show that the molecular orientation does not remain in the RT solid phase. This indicates that the intermolecular interactions are stronger than the coupling with the magnetic field. A rough estimation of the anisotropy of the diamagnetic part of χ_m shows that the paramagnetic and the diamagnetic contributions have similar values, so the total anisotropy of χ_m is low in the Cu5 case.

The evolutions of the EPR spectrum of the VO5 compound during the heating and cooling cycles in the presence of a magnetic field are roughly similar, with some noticeable differences. In the high-temperature nematic phase the EPR spectrum (see figure 5(*b*)) only shows the perpendicular features of the type I $(VO)^{2+}$ signal. It can be interpreted in a similar way to the V5 signal in the isotropic liquid phase. The VO5 molecules are able to rotate freely and are oriented through the magnetic interaction. The differences arise when the samples are cooled in the presence of a magnetic field. The RT spectrum shows no anisotropy and coincides with that obtained by cooling the sample from 250 °C in zero applied magnetic field. So in the VO5 case the orientation of the molecules reached at high temperatures does not remain in the solid phase. On the other hand the EPR spectra in the S_{crys} phase consist of rather broad lines. Although a deeper study of the magnetic properties in this S_{crys} phase is needed, these results suggest that in the VO5 case the intermolecular interactions are stronger than those in the V5 compound, and that they work against the orientation induced by the magnetic field.

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